THERMO-ANALYTICAL / NON-ISOTHERMAL STUDIES ON DECOMPOSITION OF CALCIUM CARBONATES

by

D. M. A. KHAN

THERMO-ANALYTICAL / NON-ISOTHERMAL STUDIES ON DECOMPOSITION OF CALCIUM CARBONATES

A Thesis Submitted
In Partial Fulfilment of the requirements
for the Degree of
MASTER OF TECHNOLOGY

by

D. M. A. KHAN
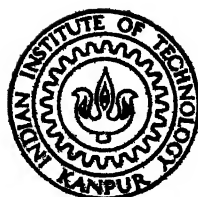
to the
DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
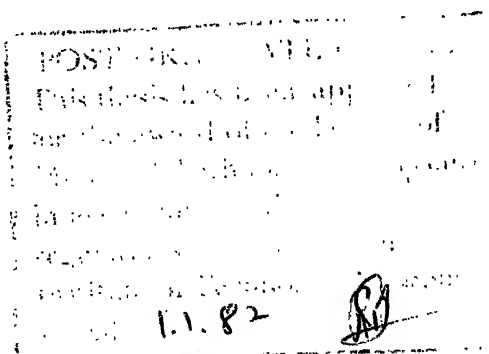DECEMBER, 1981

DEDICATED TO MY MOTHER

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C E R T I F I C A T E

This is to certify that the thesis entitled 'THERMO-
ANALYTICAL/NON-ISOTHERMAL STUDIES ON DECOMPOSITION OF CALCIUM
CARBONATES' submitted by Mr. D.M.A. Khan, in partial fulfil-
ment of the requirements for the Degree of Master of
Technology at the Indian Institute of Technology, Kanpur
is a record of bonafide research work carried out under my
supervision. The work embodied in this thesis has not been
submitted elsewhere for a degree.

Date : 28-12-81.

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ACKNOWLEDGEMENTS

C O N T E N S

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A B S T R A C T

This thesis describes about an investigation on the dissociation behaviour of a large number of samples of calcite, limestone and dolomite available in the laboratory or obtained from the industry. The industrial samples represent raw materi-als from different mines. The work has three main parts,

    (a) Development of various laboratory techniques to be applied in the investigation of decomposition reaction.

    (b) Actual studies on various samples and collection of data.

    (c) Analysis of all experimental data for quantitative assessment of the mode of decomposition and thermal properties of samples and an attempt to corelate the data obtained using different techniques.

The emphasis of the work is on the development of the experimental techniques and methodology. The experimental data have been primarily used to establish the validity of the techniques proposed and used. However, an attempt is also made to generate some decomposition data which may be of interest to the industries.

The experimental techniques described include the following,

    (a) Thermal analysis of samples (simultaneous DTA, TG, DTG).

    (b) A new technique called the 'Moving Bed' technique in which a bed length of sample is gradually introduced into a furnace hot zone and decomposition allowed to

CHAPTER I
INTRODUCTION

1.1 General :-

Limestone is recognised as an important raw material for the manufacture of Iron and Steel. It also finds use in the manufacture of portland cement, in agricultural purposes etc. An average of 0.3 ton or more of limestone flux is required to produce one ton of pig iron in blast furnace to combine principally with silica and alumina to form low melting point slags and to provide slag basicity to control silicon, sulphur and manganese levels in the molten metal. In steel making, calcinned lime is normally used as fluxing material. Limestone additions in the open hearth process gives rise to lime boil which effectively stirs the bath and brings the lime to slag where it replaces the oxides of iron and keep sulphur and phosphorus. level low. In modern rapid oxygen converters lime quality plays a critical role as it must dissolve in the slag rapidly for better control of sulphur and phosphorus. In de-oxidation of steel de-oxidising power of ferro alloys is improved by presence of CaO in the slag.

Dissociation behaviour of limestone in the burden affects the performance of blast furnaces [1]. Dissociation behaviour is also important in the calcination operations in the kiln or shaft to produce lime. It is thus important to study the decomposition behaviour of limestone.

1.2 Thermodynamics of Limestone dissociation : -

Reliable thermodynamics data for limestone decomposition are available in the literature [2]

$$CaCO_3 = CaO + CO_2; \quad \cdot \Delta G^0 = 40250 - 34.4T \quad (1)$$
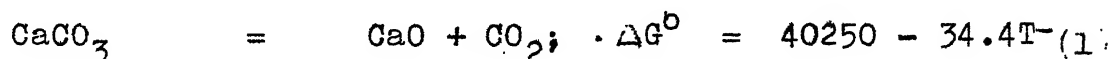
$$\Delta G^0 = - RT \ln pCO_2 \quad -- \quad (2)$$

where ΔG^0 is the standard free energy change for the reaction, pCO_2 is the partial pressure of CO_2 and T is the temperature in ^0K.

$$MgCO_3 = MgO + CO_2; \quad \Delta G^U = 28100 - 40.6T \quad -- \quad (3)$$
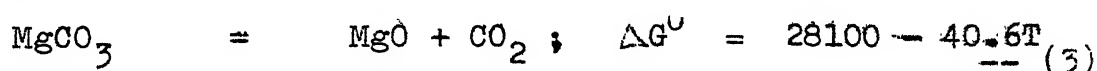
It may be readily shown that $MgCO_3$ decomposes at a temperature of 420^0C and $CaCO_3$ at 900^0C at pCO_2 of 1 atm.

In the case of dolomite the dissociation reaction would involve two sequential steps. $MgCO_3$ in dolomite decomposes first followed by $CaCO_3$. Often these sequential steps overlap.

1.2.1 Dissociation behaviour of actual Calcium carbonates :

For Calcite, dissociation temperature is 898^0C [3,4] at 1 atm. Magnesium carbonate dissociates at a much lower temperrature i.e. 420^0C at pCO_2 of 1 atm. Since the proportion of $MgCO_3$ and $CaCO_3$ differs in many species of dolomitic and magnesian limestone, the dissociation temperature naturally varies. These cannot be calculated from theory and actual experiments alone can give the data. In most cases the MgO is hard burnt in varying degrees before CaO is formed. Even if the CaO constituent is soft burnt the hard burnt MgO component influences a denser quick lime of lower reactivity than a comparably calcined high calcium lime.

According to Hedin [5], certain kinds of limestone cannot successfully calcined into lump or quick lime. These types may largely dissociate into oxide but they will decrepitate into small fractions down to dust rendering the product unsalable for many uses and seriously complicating the process of calcination. Large crystalline forms are most prone to behave like this and experimental calcination of the stone is judicious before a plant investment is made. This is 'physical oddity' and the chemical analysis of the stone has little or no influence on this characteristics.

Fostel [6] also observed that the $CaCO_3$ crystal lattice, in preheating undergoes thermal expansion of 5 to 10pct. prior to calcination. A residual effect of this expansion is an increase in the stones porosity.

1.3 Non-isothermal kinetics :-

During heating a carbonate may decompose continuously and therefore, the dissociation reaction is essentially a noniso thermal. Such reactions can be studied by thermal analysis under rising temperature conditions. Dynamic nonisothermal kinetic studies are carried out by allowing a reaction to take place at progressively higher temperature using a welldefined temperature time relationship, progress of the reaction being recorded (eg. as weight change) against temperature or time.

Traditional kinetic studies involve a series of runs in which a reaction takes place under 'isothermal conditions'.

From the plot of fraction decomposed i.e. 'α' against time 't' a reaction rate constant is derived by expressing weight as an appropriate function of 't'. If the experiment is then repeated at several other temperatures and an unchanged reaction is assumed then an Arrhenius type plot can be obtained and the activation energy calculated. Such isothermal experiments generally yield a value of about 50 Kcal/mole [7] for the activation energy of limestone.

The isothermal experiments require large number of runs. Moreover it is always difficult to attain a fixed temperature without some pre-reaction. Therefore an uncertainty remains regarding zero time of reaction. Also it is very difficult to reproduce physical characteristics of a sample in every run.

The commercial thermal analysis equipments use very small samples to ensure thermal equillibrium with the furnace. It is however possible to design a technique for thermogravimetry on large masses. The technique is described in detail later.

1.4 Differential Thermal Analysis (DTA), Thermogravimetry(TG) and Derivative Thermogravimetry (DTG)

DTA measures heat effects in a system due to phase changes or reactions. DTA studies have found wide applications in various fields. It is, however, now realized that more useful information is obtained when DTA is combined with TG and DTG. In TG the weight of the sample is measured continuously and the course of the reaction is followed through measuring weight changes.

DTG gives the rate of change of weight loss and gives a measure of reaction rate at various temperatures. The modern approach in thermal analysis therefore is simultaneous DTA, TG and DTG studies. The principles of these techniques are well known and therefore will not be dicussed here.

1.5 Aim of the present Investigation :-

The present work is aimed at studying decomposition behaviour of a large number of calcite, limestone and dolomite samples using various techniques of thermal analysis. The techniques include DTA, TG, DTG and a new method called 'Moving Bed' technique which is suitable for studying the decomposition behaviour of large samples. They are described in detail in subsequent chapters.

The data obtained using various techniques are to be analysed to establish an overall comparison of the decomposition behaviour of various samples.

CHAPTER II
PLAN OF THE WORK

The present work is aimed at comparing the dissociation behaviour of various grade samples of calcite, limestone and dolomite under Isothermal/Non-isothermal experimental conditions. The work is contemplated in the following manner.

2.1 DTA Technique :-

DTA technique is suitable only for very small samples (10 to 500 mg) to investigate exothermic or endothermic reactions taking place in the system. TG shows whether the reactions involve weight changes or not. DTG gives additional kinetic data for the reaction by providing the slope values of TG curve. A standard 'Derivatograph' instrument was used for simultaneous measurements of DTA, TG and DTG of the samples.

First the effect of parameters such as particle size, heating rate, gas flow rate etc. was established. Subsequently all studies were done under standardized conditions so that the experimental data become amenable for comparative analysis. A series of experiments were also conducted to study sequential decomposition reactions such as those found in a combination of carbonates. The effect of the nature of association of carbonates was studied.

2.2 Moving bed technique :-

This method describes a generalized approach on non-isothermal kinetic investigations which use large samples and non-

linear heating programme. It proposes a moving bed experiment in which a large volume of sample is spread in a long quartz tube and the tube is introduced into a furnace hot zone at uniform speed. When the boat is withdrawn, it gives a series of successive volume elements which have been subjected to a temperature-time programme for different periods.

The heating programme would depend primarily on the temperature profile of the furnace, the boat speed and the heat transfer co-efficient. The temperature-time plots can be obtained by thermocouples positioned in the moving bed for several samples. The results of such findings established non-isothermal kinetic data for a known heating programme. It was then possible to compare the dissociation of large and small samples.

2.3 Measurement of evolution of Carbon di-oxide :-

An apparatus was set up to measure the flow rate of liberated CO_2 gas which in turn could be related to the amount of material decomposed at any time of heating. Variables studied in such experiments include temperature, CO_2 pressure, particle size, different grade of materials etc.

In some experiments simultaneous temperature and carbon di-oxide measurements were carried out to give additional information on the decomposition behaviour of samples.

CHAPTER III
EXPERIMENTAL

3.1 Materials :-

For thermal analysis most of the samples were obtained from Bokaro Steel Limited, Bokaro (samples of limestone and dolomite) brought from the sources such as Kuteshwar, Satna, Chopan, Birmitrapur, Baradwar, Ramtek etc. Double carbonates of $Na_2CO_3 \cdot CaCO_3$ were synthesized in the laboratory. Calcite and locally available limestone and dolomite. materials were procured and chemically analysed in the laboratory and the compositions are given in Table III-1. Analytical grade of $CaCO_3$ and $MgCO_3$ with purity of almost 99 pct. were also used in some studies.

Unless otherwise mentioned the average particle size of the samples used was 75μ(micron) i.e. -90μ to $+63\mu$ for DTA. In all other cases the actual sizes used are mentioned with all experimental data.

3.2 Equipments :-
3.2.1 Derivatograph :

The line sketch of the Derivatograph is shown in fig.(1) [8,9]. In the DTA cell there are two thermocouples interconnected through a galvanometer. One crucible holds the reference material Al_2O_3(Alumina) and the other holds the test sample. The two crucibles are heated in a furnace. There is provision for flushing the system with inert gas argon at a controlled flow rate. The equipment offers various sensitivities and various rates of heating are available (e.g. 5°, 10°, 25°, 30^oC/min.)

T A B L E III - 1

CHEMICAL ANALYSIS OF SAMPLES AFTER COMPLETE BURNING

AT 1000°C

Compounds	Calcite pct.	Limestone pct.	Dolomite pct.
CaO	98.57	84.34	70.42
MgO	...	4.72	24.51
SiO_2	1.27	6.19	1.31
Fe_2O_3	0.16	4.01	2.61
Al_2O_3	..	0.74	1.14

INERT
SUBSTANCE

SAMPLE

SAMPLE HOLDER
(FURNACE)

+   −   −   +

THERMO COUPLE
No. 2

THERMO COUPLE
No. 1

GALVANOMETER
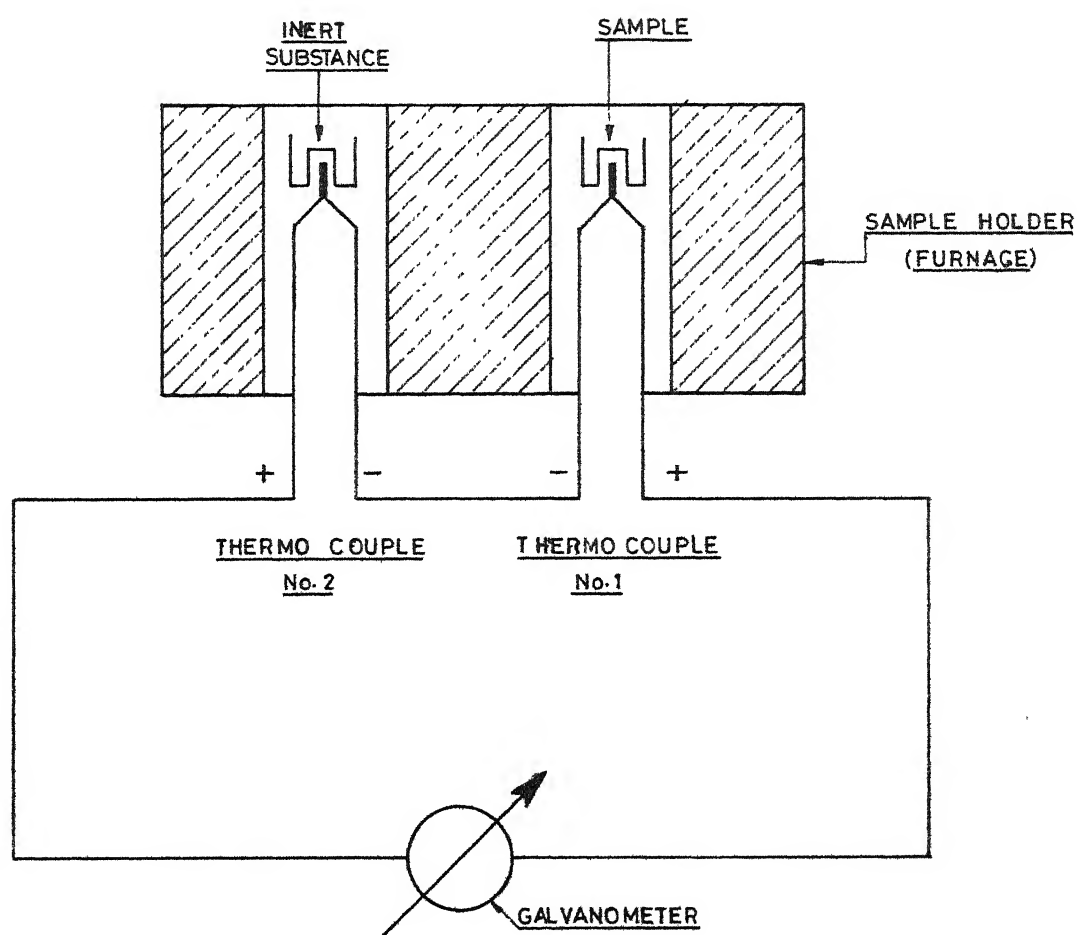
FIG(1) LINE SKETCH OF DERIVATOGRAPH

3.2.2. Moving bed and other Experiments:-

For moving bed and CO_2 evolution studies, a kanthal wound resistance furnace was employed. A sketch of the apparatus is shown in fig.(2). The temperature was controlled with an accuracy of $\pm 5^{\circ}C$ with the help of a temperature controller. Actual temperature was measured using a Chromel-Alumel thermocouple connected to a potentiometer. The rate of evolution of CO_2 was controlled through a mercury bubbler device shown in fig.(3). and by using a capillary flowmeter.

3.3 Experimental Procedure :-

3.3.1 DTA/TG/DTG plots :

About 400 mg of the sample was taken in a standard ceramic crucible and kept above Thermocouple No.1. Inert Al_2O_3 sample was taken in the other crucible and kept above the thermocouple No.2. The standard flow rate of argon was 1cc/min. DTA, TG and DTG plots were plotted simultaneously. The details of the experimental conditions for the thermal analysis studied in the present work are given in Table-III-2.

3.3.2 Moving bed technique :

About 100 gm of calcite in the size range of -5 to +14 mesh were dried in an oven and kept inside a 60cm long, 1.4cm I·D·, quartz tube which was sealed from one end. The tube was then pushed inside the furnace at the rate of 1 cm/min or 1/2 cm/min for a predetermined period of time, removed and allowed to cool in air. The material was sampled from various distances along the length of the tube for further analysis by reheating the volume elements individually at $1000^{\circ}C$ for 90 minutes.
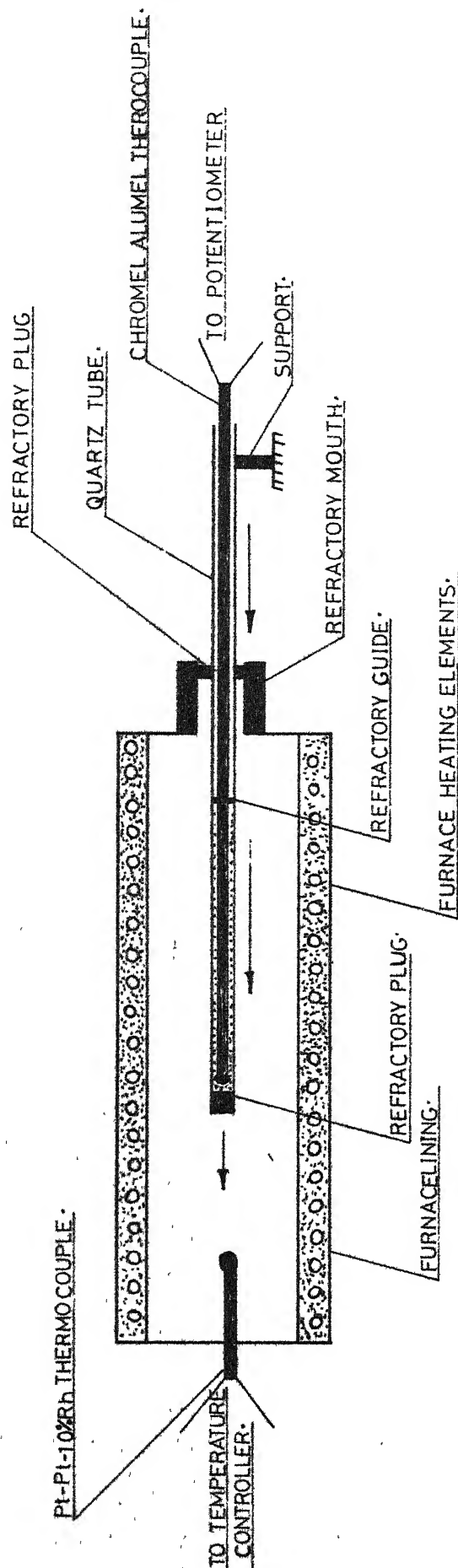
FIG.(2) SCHEMATIC DIAGRAM OF
MOVING BED APPARATUS.

REFRACTORY PLUG

QUARTZ TUBE.

CHROMEL ALUMEL THEROCOUPLE.

TO POTENTIOMETER.

SUPPORT.

REFRACTORY MOUTH.

REFRACTORY GUIDE.

FURNACE HEATING ELEMENTS.

REFRACTORY PLUG.

FURNACELINING.

Pt-Pt-10%Rh THERMO COUPLE.

TO TEMPERATURE
CONTROLLER.
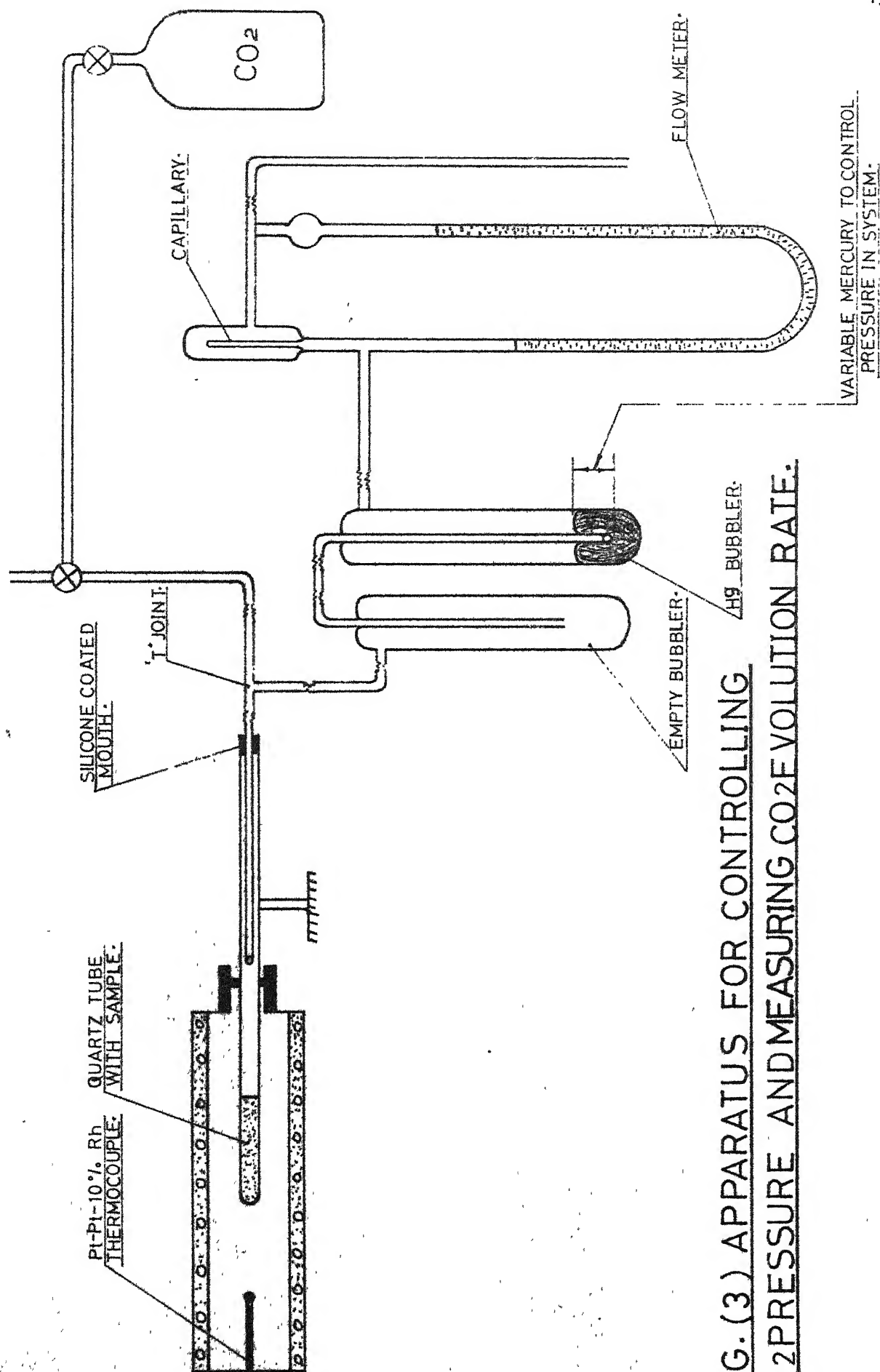
FIG. (3) APPARATUS FOR CONTROLLING
CO2 PRESSURE AND MEASURING CO2 EVOLUTION RATE.

3.3.3 Measurement of Carbon di-oxide evolution :-

About 25 gm of sample after drying was kept in the quartz tube which was connected through a mercury pressure regulat- to a calibrated capillary flowmeter as shown in fig.(3). The apparatus was first purged by passing CO_2 from cylinder for abo 10 minutes. Then the tube was introduced well inside the fur- nace and CO_2 liberated was measured at regular interval of time. The experimental details of various experiments carried out are given Table III-3.

3.3.4 Temperature measurements in Static bed :-

In another set of experiments, a chromel-alumel thermocou- ple was placed at the centre of sample (25 gm) and the quartz tube containing the sample was kept well inside the furnace and temperature was measured at regular interval. In some experi- ments attempts were made to measure the temperature and the flo rate of liberated CO_2 simultaneously.

3.3.5 Temperature measurements in Moving bed :

A chromel-alumel thermocouple was fixed at a known dista- nce inside the tube containing sample (50 gm) as shown in fig.(3) The mouth of refractory plug in the furnace tube was taken as the reference for measuring distances in all the cases. The tube was pushed inside the furnace manually at the increments of 1 cm/min and the temperature was measured at 30 sec. interval. And the details of experimental conditions are given in Table III-4.

T A B L E - III-3

DETAILS OF EXPERIMENTAL CONDITIONS FOR CO_2 EVOLUTION

MEASUREMENTS

Expt.No.	Material	Amount (gm)	Control Temp. °C	CO_2 Partial Pressure(atm)	Particle size (mesh)	Total Exptl Time(m)
CE0	Calcite	31.19	1000	1.03	-5 to +14	40
CE1	''	31.11	''	''	''	35
CE2	''	27.21	''	''	''	25
CE3	''	26.92	''	''	-48 to +65	30
CE4	''	27.69	''	''	-14 to +20	
CE5	''	27.26	''	''	+3	25
CE6	L/S-CNB	28.04	''	''	-14 to +20	20
CE7	''	32.23	''	''	+3	20
CE8	Dolo-CNB	28.91	''	''	-14 to +22	20
CE9	Calcite	27.28	''	1.25	-5 to +14	35
CE10	''	26.76	''	''	''	35
CE11	''	26.27	''	1.5	''	45
CE12	''	29.42	''	1.5	''	45
CE13	L/S-CNB	27.33	''	''	-14 to +20	30
CE14	Calcite	29.11	980	1.03	-5 to +14	45
CE15	''	29.65	980	''	''	50
CE16	''	29.88	950	''	''	50
CE17	''	32.17	''	''	''	60
CE18	''	30.96	''	''	''	60
CE19	''	28.69	''	1.03	-5 to +14	60
CE20	L/S-CNB	26.59	''	''	-14 to +20	90
CE21	L/S-CNB	31.91	''	''	+3	40
CE22	Dolo-CNB	26.18	'	''	-14 to +22	40
CE23	Calcite	27.43	''	1.25	-5 to +14	40
CE24	L/S-CNB	27.82	''	1.5	-14 to +20	60
CE25	Calcite	28.32	925	1.03	-5 to +14	60
CE26	''	25.48	900	1.03	-14 to +20	60
CE27	L/S-CNB	25.55	''	''	-14 to +20	90
CE28	''	32.42	''	''	+3	60
CE29	Dolo-CNB	29.10	''	''	-14 to +22	30
CE30	L/S-CNB	27.37	''	1.5	-14 to +20	60
CE31	''	28.19	850	1.03	''	20
CE32	''	31.22	''	''	-14 to +22	35
CE33	Dolo-CNB	28.61	''	''	''	30
CE34	L/S-CNB	27.82	''	1.5	-14 to +20	45
CE35	Dolo-CNB	28.76	800	1.03	-14 to +22	60
CE36	''	28.68	750	1.03	''	60

T A B L E III-4

EXPERIMENTAL CONDITIONS FOR TEMPERATURE MEASUREMENTS

IN STATIC AND MOVING BEDS

Maximum Time = 30min   Controller Temperature = $1000^\circ C$
Bed Speed   = 1cm/min   Sample length-Static   = 10 cm
                          Sample length-Moving   = 20 cm

Expt. No.	Material	Size(mesh)	Position of Thermocouple	Remarks
TM1	Empty tube	..	-5 cm	Static bed
TM2	Calcite	-5 to +14	-5 cm	" "
TM3	L/S-CNB	-14 to +20	" "	" "
TM4	Dolo-CNB	-14 to +22	" "	" "
TM5	Empty tube	..	0	Moving bed
TM6	" "	..	-10 cm	" "
TM7	" "	..	-20 cm	" "
TM8	" "	..	-27 cm	" "
TM9	Calcite	-20 to +28	0	" "
TM10	" "	" "	-5 cm	" "
TM11	" "	" "	-10 cm	" "
Tm12	" "	" "	-18 cm	" "
TM13	" "	" "	-22 cm	" "
TM14	L/S-CNB	-14 to +22	0	" "
TM15	" "	" "	-5 cm	" "
TM16	" "	" "	-10 cm	" "
TM17	" "	" "	-18 cm	" "
TM18	" "	" "	-22 cm	" "
TM-CE19	Calcite	-20 to +28	-5 cm	Static bed
TM-CE20	L/S-CNB	-14 to +22	-5 cm	" "

C H A P T E R   IV

R E S U L T S

4.1 Results of Derivatograph experiments :-

Results of DTA, TG and DTG experiments i.e. from DT1 to
DT18 as obtained from derivatograph are summarized in Table IV-1.
The exact plots for some experiments are given in figures from
(4) to(13). In samples of dolomite i.e. in experiments DT5 and
DT6, weight losses due to calcination of $MgCO_3$ and $CaCO_3$ are
found separately from the TG plots and these results are marked
as 'A' and 'B' respectively in Table IV-1.

4.2 Results of calcite decomposition in Moving bed experiments:-

The results of experiments carried out using moving bed
techniques as described in section 3.3.2 for non-isothermal
decomposition studies of calcite are given in Table IV-2.

4.3 Results of experiments measuring evolution of Carbon dioxide in Static beds :-

Table IV-3 gives the results of experiments to measure
evolution of CO_2. The details of those experimental conditions
such as pCO_2, sample weight, source etc., have been given in
Table III-3. Typical plots for the rate of CO_2 evolution for
materials like calcite, limestone and dolomite are given fig.(14).
Limestone and dolomite decompose rather easily than calcite.
It may be noted that total area under the curve upto certain
duration would give total amount of CO_2 liberated in that

r ... . it .... b. ....

T A B L E   IV-1

RESULTS OBTAINED BY TG PLOTS SHOWING WEIGHT LOSSES

AT VARIOUS TEMPERATURES IN DT EXPERIMENTS

Run No.	Weight loss in mg at Temperature °K							Maxm. wt. loss(mg)	Maxm. pct. wt. loss calculate
	873	973	1073	1173	1213	1253	1273		
DT1	..	..	4	28	50	100	126	155	39.14
DT2	..	1	4	30	60	110	156	161	40.25
DT3	1	4	12	44	85	116	136	140	35.00
DT4	..	..	2	28	58	108	138	152	38.56
DT5'A'	..	8	17	86	..	..	..	90	22.50
DT5'B'	..	..	..	..	78	88	101	102	25.50
DT6'A'	..	7	14	..	..	..	..	70	17.50
DT6'B'	..	..	..	30	58	92	102	104	26.00
DT7	..	2	4	25	52	87	122	126	32.47
DT8	96	104	112	154	188	190	192	192	48.00
DT9	..	1	2	16	32	48	58	84	21.00
DT10	..	..	5	25	35	48	60	125	31.25
DT11	..	..	1	74	104	124	144	144	42.48
DT11A	100	..	..	..	..	..	..	100	57.14
DT12	..	..	1	13	34	69	104	134	33.50
DT13	..	..	4	30	50	110	135	160	40.00
DT14	..	..	3	24	36	76	115	159	39.75
DT15	..	..	3	20	39	68	97	140	35.00
DT16	..	..	1	11	27	73	123	140	35.00
DT17	..	..	1	21	49	126	144	162	40.50
DT18	..	..	1	20	50	102	154	162	40.50
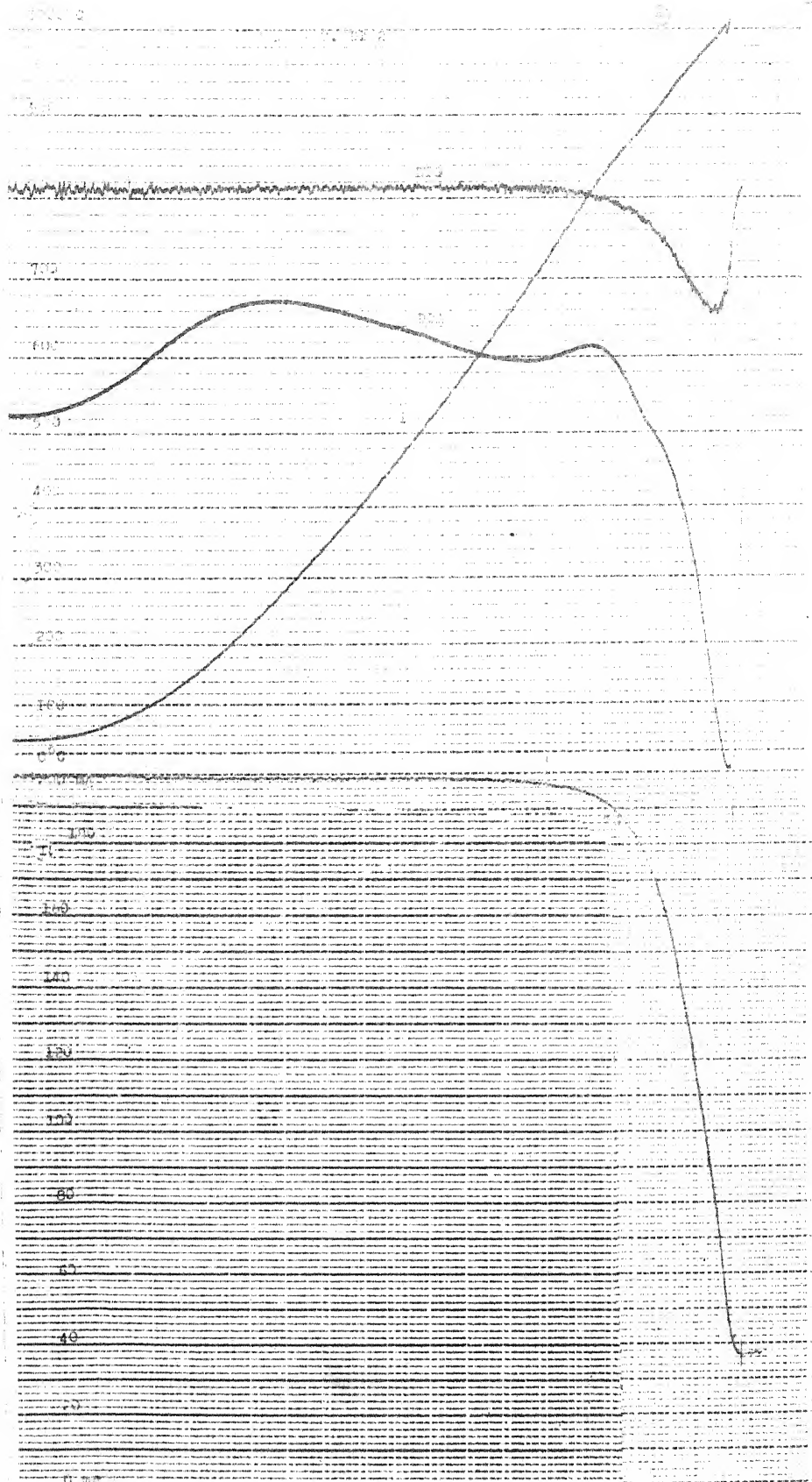
Fig.(4) DTA/TG/DTG/T PLOTS FOR LIMESTONE FROM SATNA

21
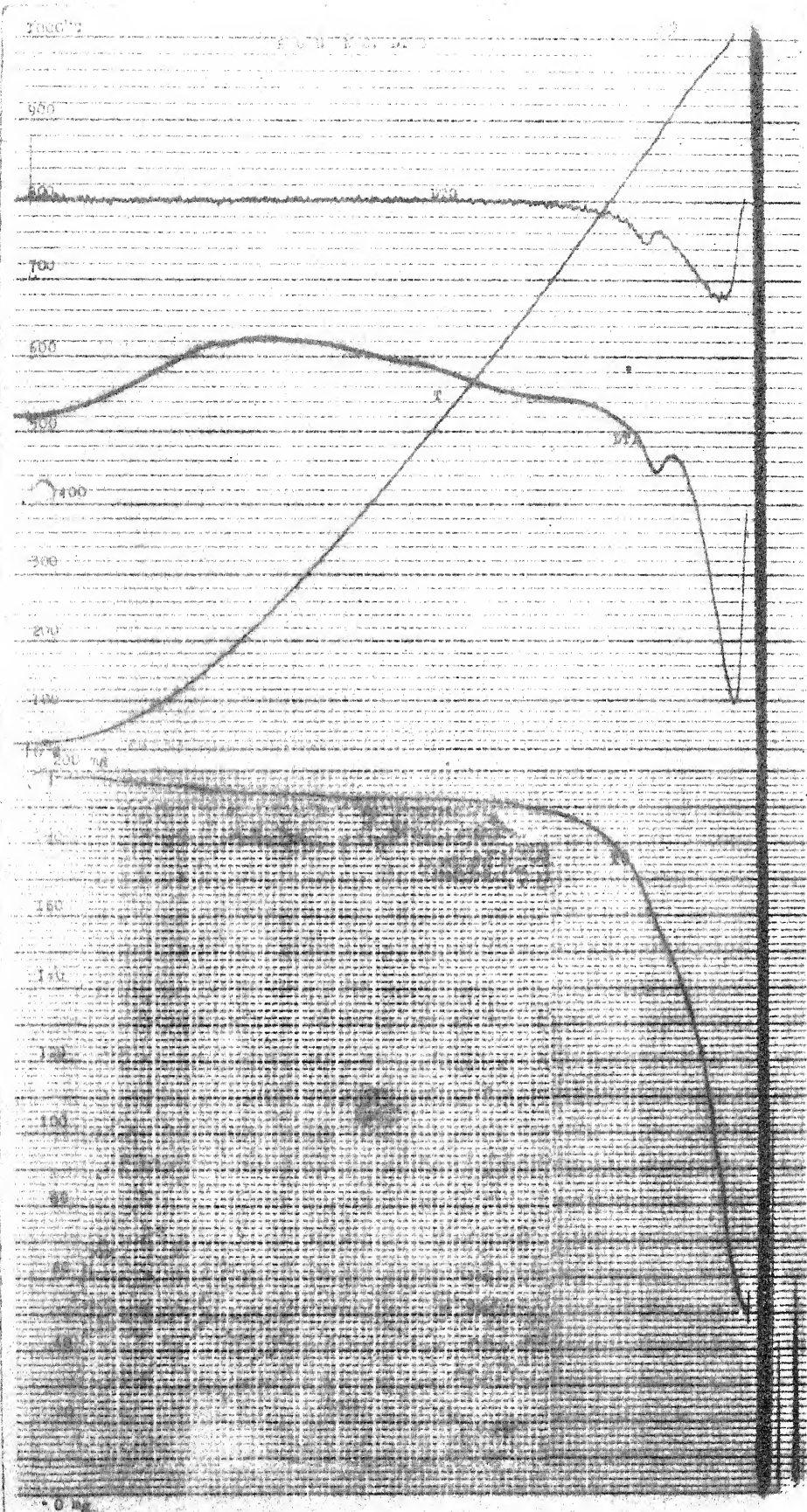
Fig. (5) DTA/TG/DTG/T PLOTS FOR LIMESTONE FROM CHOPAN
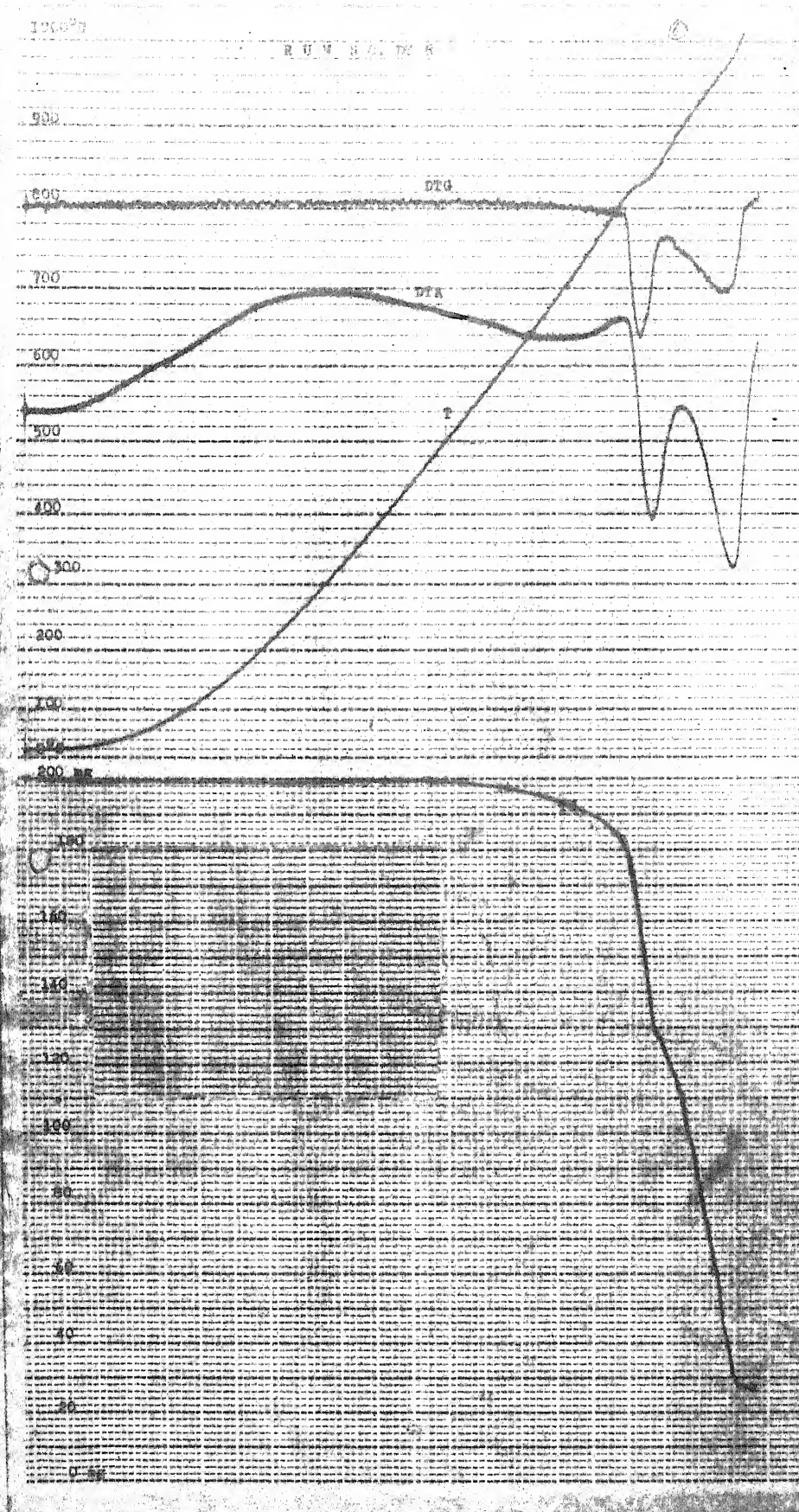
Fig. (6) DTA/TG/DTG/T PLOTS FOR DOLOMITE FROM HAMTEY
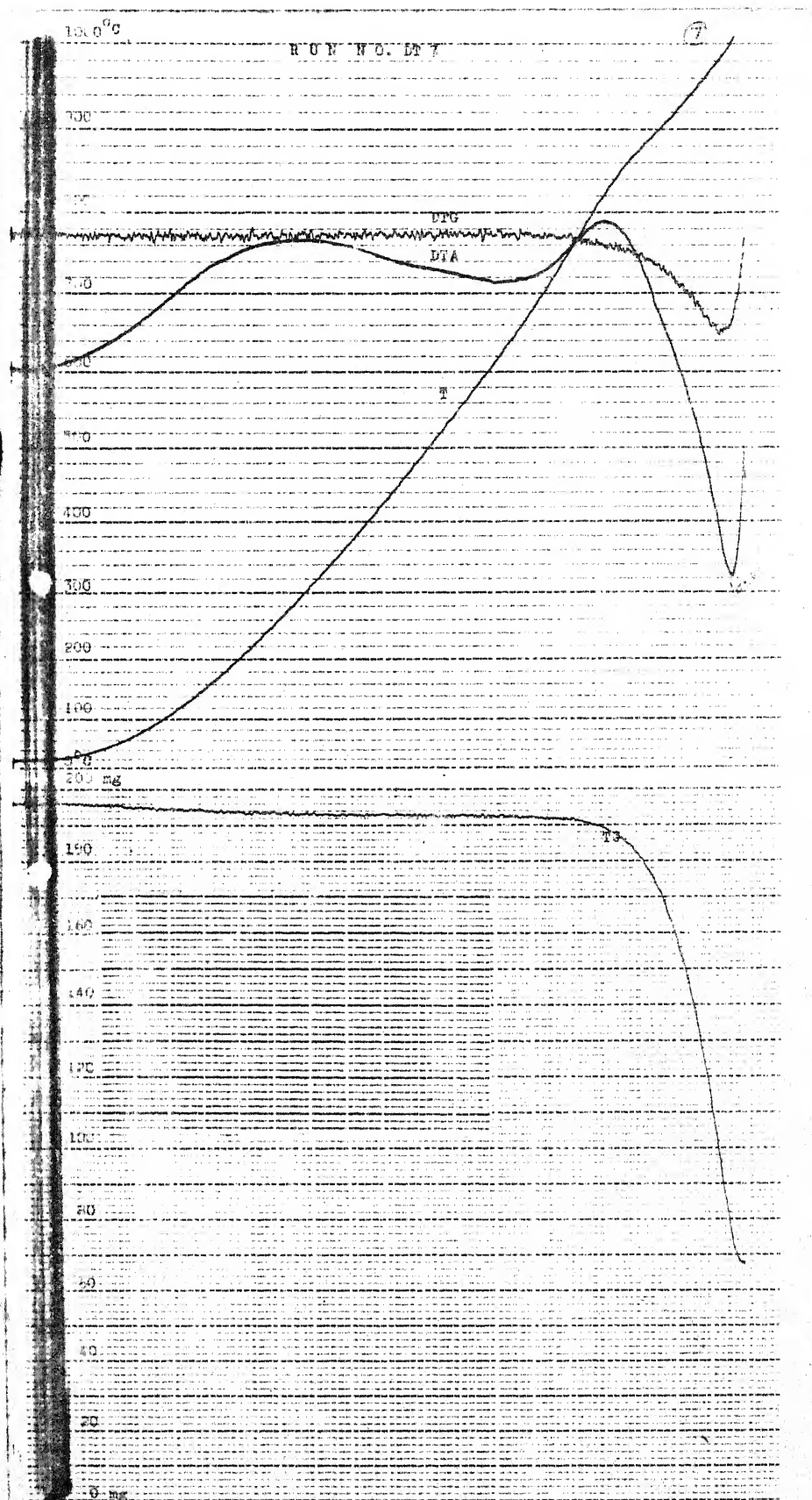
(Fig. (7) DTA/TG/DTG/T PLOTS FOR DOLOMITE FROM CHOPAN
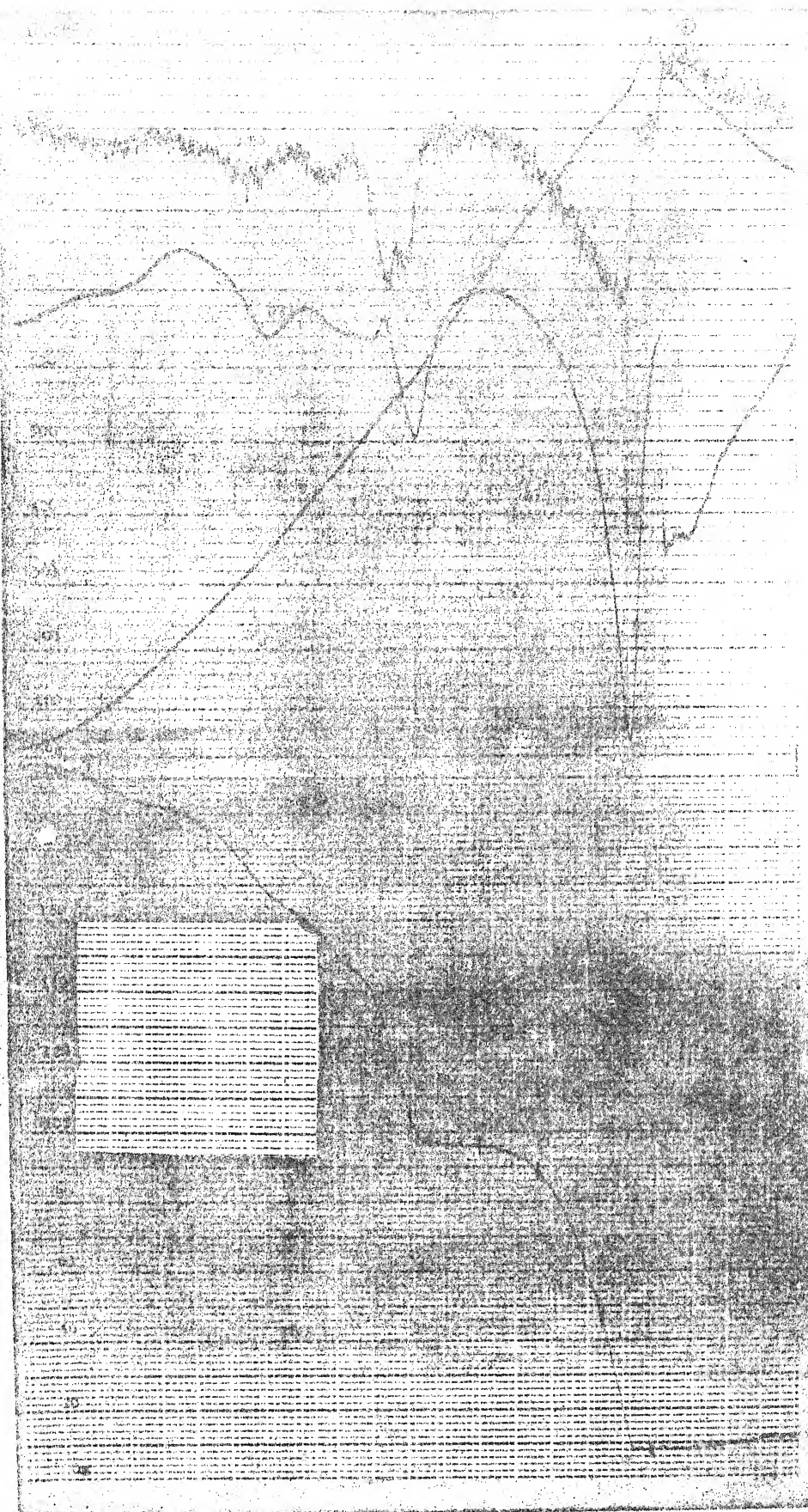
Fig. (8) DTA/TG/DTG/T PLOTS FOR MECHANICAL MIXTURE OF $CaCO_3$ AND $MgCO_3$
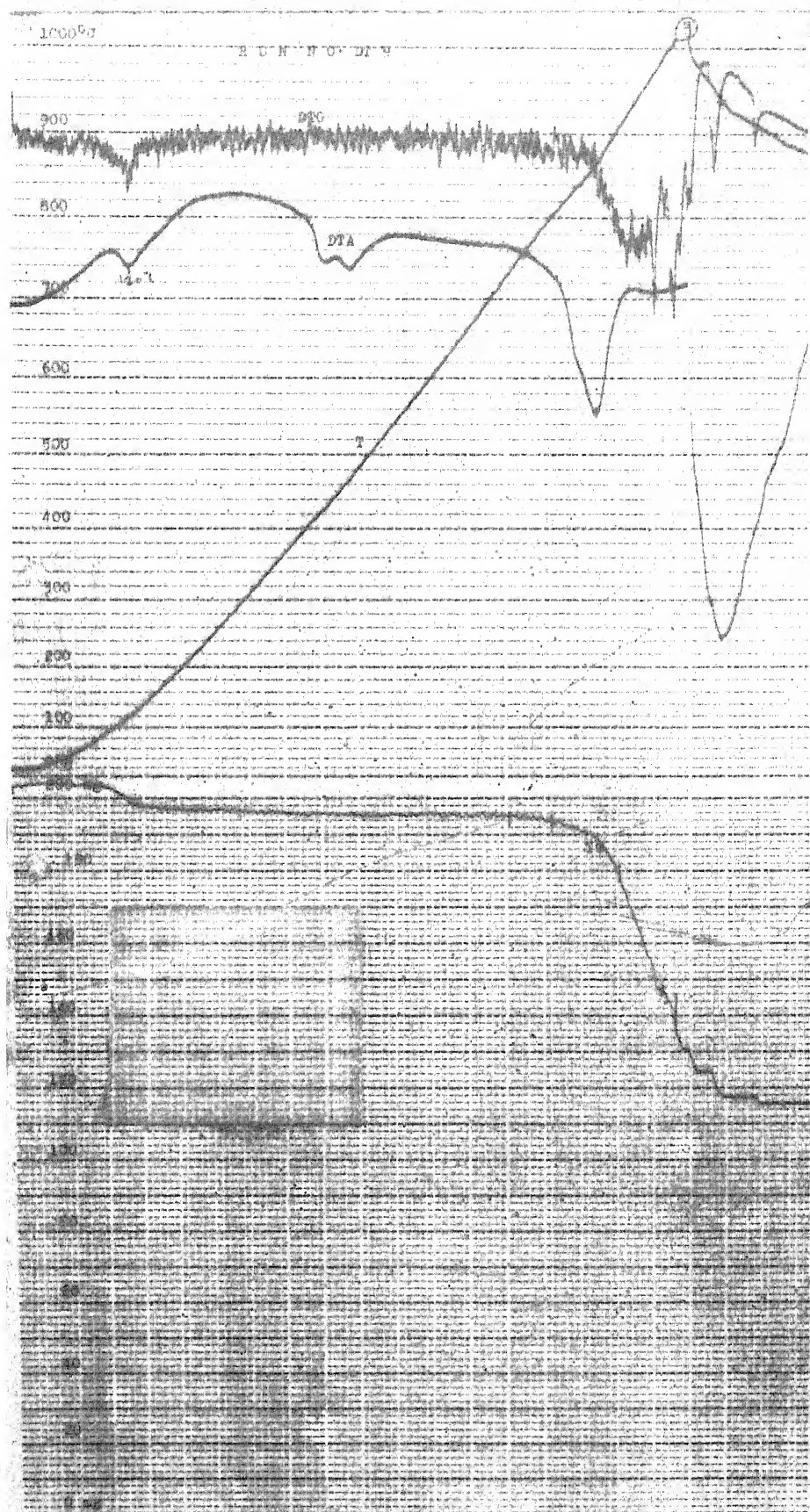
Fig. (9) DTA/TG/DTG/T PLOTS FOR DOUBLE CARBONATE
$(Na_2CO_3. CaCO_3)$
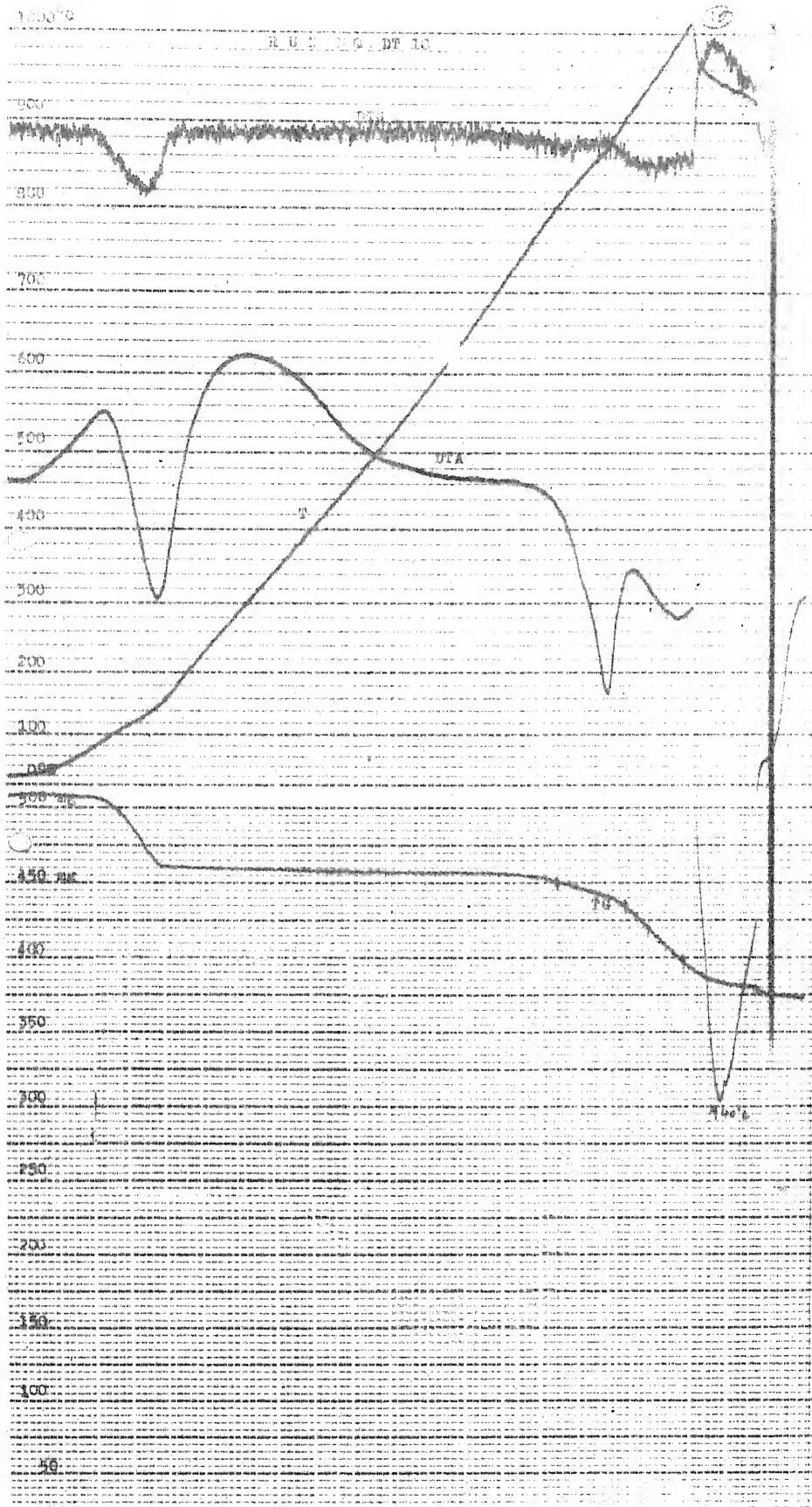
Fig. (3.10) DTA/TG/DTG/T PLOTS FOR MECHANICAL MIXTURE OF
Na_2CO_3 AND $CaCO_3$)
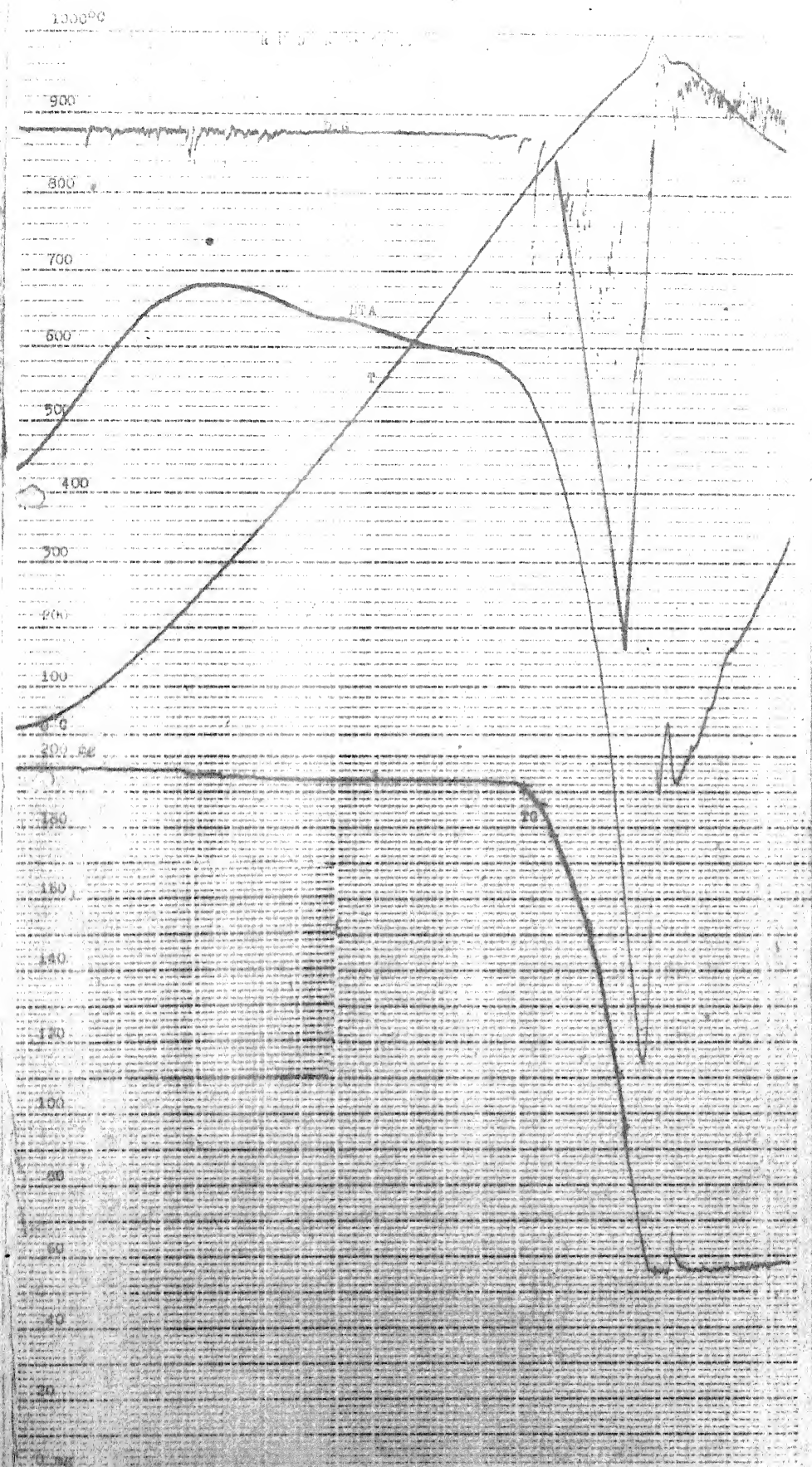
Fig. (11) DTA/TG/DTG/T PLOTS FOR PURE CaCO₃ (A/R Grade)

28

1000°C

RUN NO- DT 11A

900   DTG

800

700

600   DTA

500

T

400

300

200

100

450

400   TG

350

300

250

200

150

100

50

p ms

Fig. (12) DTA/TG/DTG/T PLOTS FOR PURE MgCO₃ (A/R Grade)
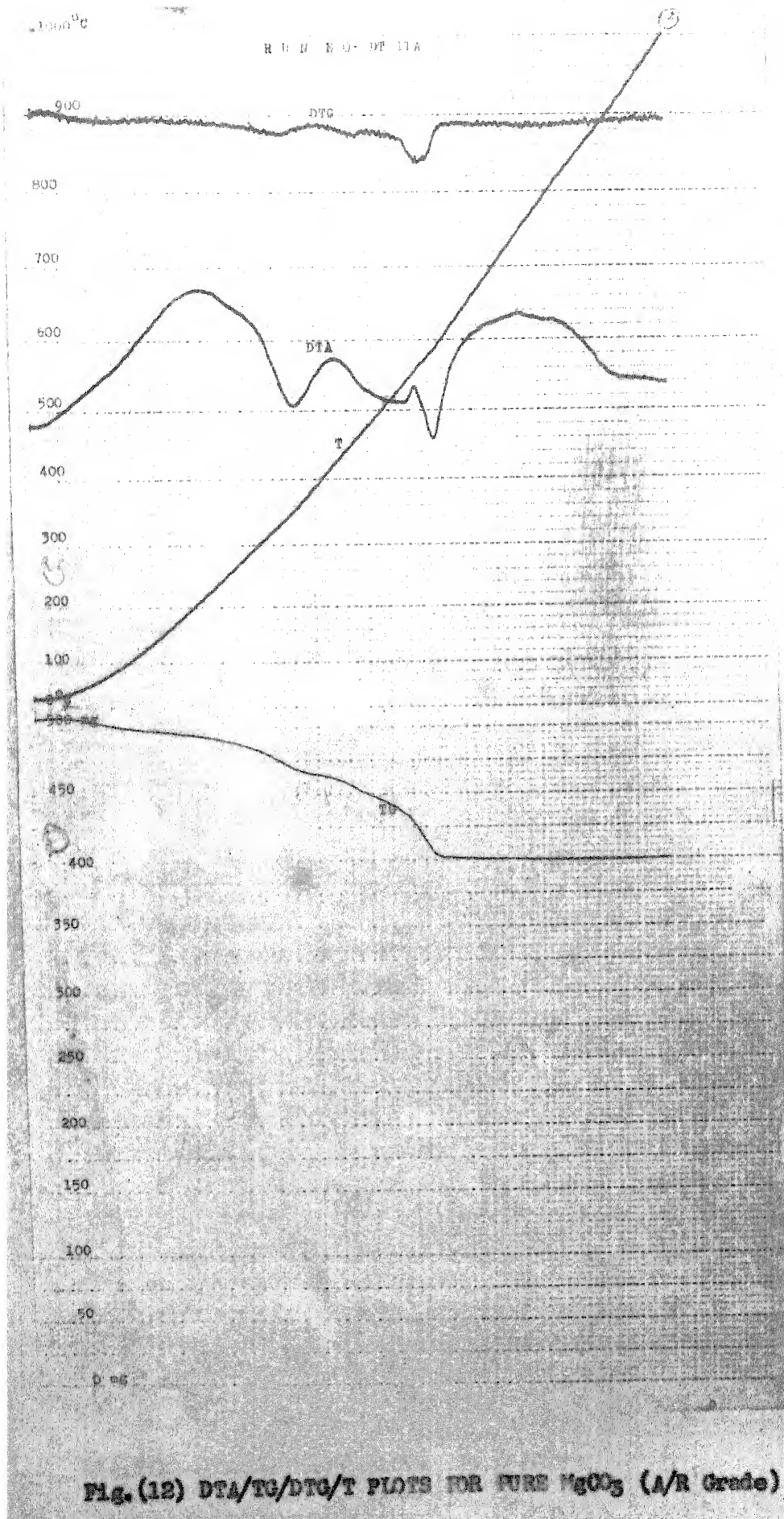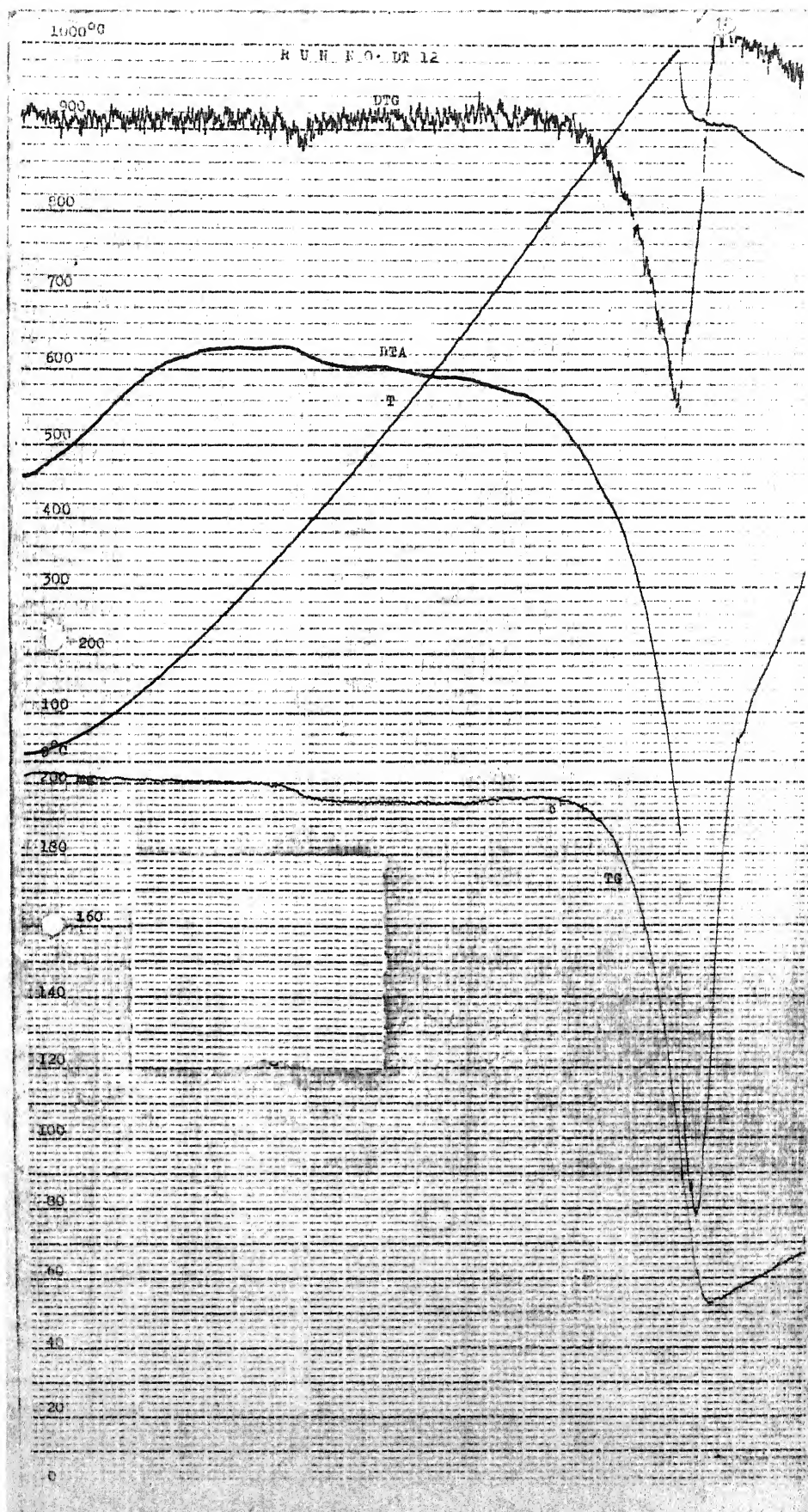
Fig.(13) DTA/TG/DTG/T PLOTS FOR CALCITE

T A B L E IV-2

RESULTS OF CALCITE DECOMPOSITION IN

MOVING BED EXPERIMENTS

Expt.No.	Maximum Temp. °C	Bed speed cm/min	Pct. loss on ignition of vol. elements collected at distances in cm of							
			0 - 3	3 - 6	6 - 9	9 - 12	12-15	15-18	18-21	21-24
MB1	911	1/2	36.61	39.39	42.99	44.56	..	..	..	..
MB2	958	1/2	24.38	34.28	36.60	39.91	39.67	40.88	43.28	43.07
MB3	1015	1/2	8.57	8.97	9.20	16.12	25.32	35.36	39.92	42.76
MB4	911	1	39.38	42.62	41.31	..	..	..	..	..
MB5	958	1	33.13	38.49	40.17	42.31	43.06	41.70	..	..
MB6	1015	1	12.83	13.56	22.41	29.62	33.31	37.78	40.65	42.28

T A B L E   IV-3

SUMMARY OF RESULTS OBTAINED FROM CO_2 EVOLUTION EXPERIMENTS

Expt. No.	Measured Temp. °C	Actual wt.loss (gm)	Actual pct. loss	*Cumulative calculated wt. loss (gm)* 5 min	10min	15min	20min	25min	30min	Measured loss (gm)	Calculated pct loss
CE0	1002	13.36	42.84	2.41	6.78	10.18	12.33	13.83	14.74	15.54	49.82
CE1	1005	13.29	42.73	2.14	5.78	10.38	12.32	13.86	12.88	13.74	44.17
CE2	902	11.48	42.17	4.09	8.24	9.65	11.12	12.06		12.06	44.32
CE3	1015	10.57	39.25	3.55	6.72	8.06	8.87	9.41	9.57	9.57	35.55
CE4	1015	11.40	42.06	2.74	6.56	8.01	9.68	10.43	10.75	10.75	39.68
CE5	1015	11.64	42.71	3.92	8.82	11.45	12.25	12.41		12.41	45.52
CE6	1015	12.06	43.00	7.50	10.99	13.00	13.27			13.27	47.33
CE7	1004	14.13	43.83	5.90	10.99	13.13	13.67			13.67	42.41
CE8	1009	13.42	46.43	11.37	15.23	16.30	16.41			16.41	56.76
CE9	996	11.28	41.35	2.48	5.90	8.58	10.39	11.73	12.66	13.27	48.64
CE10	1010	11.14	41.53	2.08	5.63	8.71	11.06	12.80	14.20	15.21	56.84
CE11	1015	10.75	40.89	1.41	4.36	6.57	8.04	9.11	9.65	12.13	46.17
CE12	1008	12.24	41.61	1.94	5.16	7.64	9.31	10.45	11.19	11.73	39.87
CE13	1008	11.92	43.62	3.55	7.17	8.98	9.78	10.18	10.32	10.32	37.76
CE14	980	12.37	42.47	1.34	4.02	6.43	8.58	10.18	11.66	14.07	48.33
CE15	978	12.38	41.75	1.54	4.96	7.44	10.45	11.79	12.80	15.08	50.86
CE16	945	11.66	39.04	1.21	2.95	4.29	5.63	6.30	6.83	11.52	38.55
CE17	943	10.08	31.35	1.21	2.95	4.82	6.70	8.31	9.65	15.87	41.33
CE18	940	12.75	41.17	0.94	2.81	4.56	6.16	7.77	9.11	16.08	51.50
CE19	950	9.67	33.69	0.54	1.74	3.42	5.23	6.37	7.24	9.65	33.63
CE20	959	11.34	42.63	2.14	4.76	6.83	7.97	8.71	9.38	9.92	37.31
CE21	955	13.85	43.33	2.95	6.43	9.38	11.52	13.13	13.50	13.80	43.25
CE22	959	12.72	45.88	5.15	9.01	11.05	12.44	13.41	13.94	14.53	55.50
CE23	958	9.40	34.27							14.07	51.29
CE24	953	11.31	40.67	2.28	4.02	5.70	6.90	7.77	8.51	10.45	37.56
CE25	923	6.41	22.40	0.97	2.68	4.29	5.15	5.42	5.57	5.57	19.67
CE26	901	0.29	1.21							0.28	1.09
CE27	908	5.13	20.06	2.01	2.35	2.41	2.48	2.55	2.61	3.42	13.39
CE28	904	5.49	16.93	1.88	2.14	2.41	2.68	2.95	3.22	4.55	14.03
CE29	901	6.78	23.20	5.00	6.22	6.76	6.92	7.24	7.56	7.56	25.98
CE30	901	2.95	10.79	2.01	2.81	2.95	3.02	3.08	3.15	3.55	12.97

T A B L E IV-3

SUMMARY OF RESULTS OBTAINED FROM CO_2 EVOLUTION EXPERIMENTS

Expt. No.	Measured Temp. °C	Actual wt. loss (gm)	Actual pct. loss	Cumulative calculated wt. loss (gm)						Measured loss (gm)	Calculated pct. loss
				5 min	10min	15min	20min	25min	30miss		
CB1	843	2.77	9.83	1.41	2.21	2.31	2.38			2.38	8.44
CB2	850	3.33	10.66	1.47	2.14	2.41	2.68	2.95	3.22	3.35	10.73
CB3	849	6.41	22.40	0.97	2.68	4.29	5.15	5.42	5.57	5.57	19.47
CB4	841	2.78	10.00	1.61	2.61	2.68	2.71	2.75	2.78	2.88	10.35
CB5	787	6.30	21.89	0.15	1.09	2.21	3.25	4.06	4.73	6.33	22.01
CB6	741	1.47	5.11	0.01	0.06	0.11	0.20	0.29	0.42	1.52	5.30

CE
22
DOLOMITE - CNB 959°C

CE
21
L/S
CNB
965°C

FIG. (14) TYPICAL PLOTS (CO₂
EVOLUTION) OF CC/SEC AGAINST
TIME FOR CALCITE, L/S, DOLOMITE·

CE 19
CALCITE 950°C

Time (Minutes)
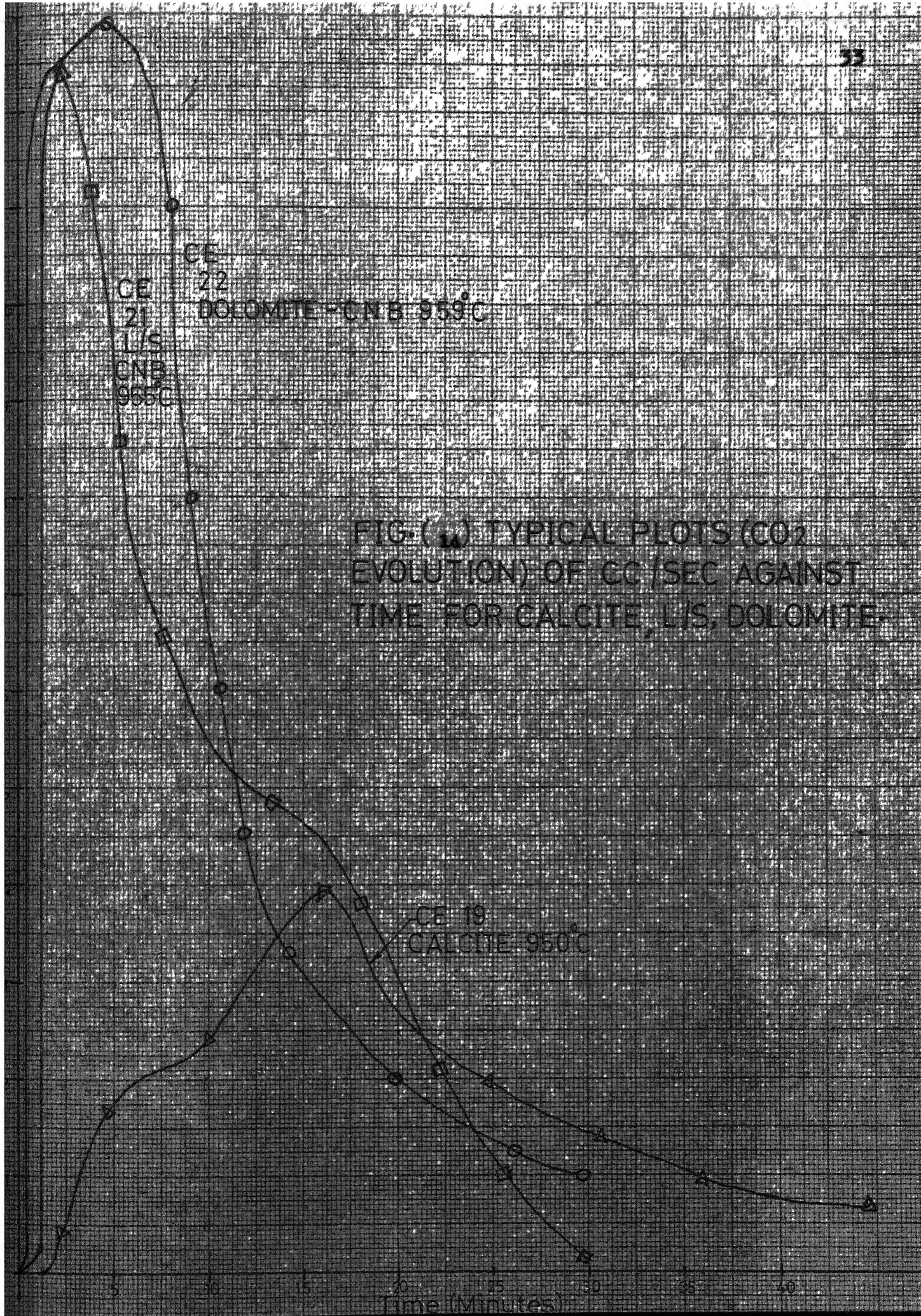
period and it can be thus related to the loss in weight of the sample as shown in fig.(15). This has been verified and confirmed by actual weighing of the sample at the end of experiments.

In those cases where the matching is not very good error is presumably in the measurement of CO_2 evolved especially in the initial stages or due to improper calibration of the flowmeter. The initial rate of evolution in some cases especially with limestone and dolomite was very large could not be determined accurately. Weight loss data for such experiments are suitably corrected by simple additions, substractions or by multiplications by comparing the actual weight loss of sample with measured weight loss from CO_2 evolution plot at the end of experiments. The corrected dat are summarized in Table IV-4.

4.4 Temperature measurements on heating of Static bed (Results):-

Fig.(16) shows the results of temperature measurements f calcite, limestone and dolomite in static beds contained in tubes. For comparison purposes, temperature response of the thermocouple in empty tube is also plotted in the fig.(16). The results of the simultaneous measurement of temperature and CO_2 evolution are given in fig.(17).

4.5 Results of measurement of temperature during Moving bed experiments :-

A number of experiments were carried out to understand the variation of temperature with time to different volume elements in a moving bed when the tube was introduced into the furnace under a given set of conditions. The reults of temperature measurements in empty tube, for calcite and limestone (TM5 to TM18) of Table III-4 are described in figures (18), (19) and (20).

FIG. (1b) OUT-LINE OF RESULTS ON CO₂ EVOLUTION EXPERIMENTS.

○ ACTUAL % WEIGHT LOSS
◁ CALCULATED % WEIGHT LOSS
C = CALCITE
L = L/S
D = DOLOMITE
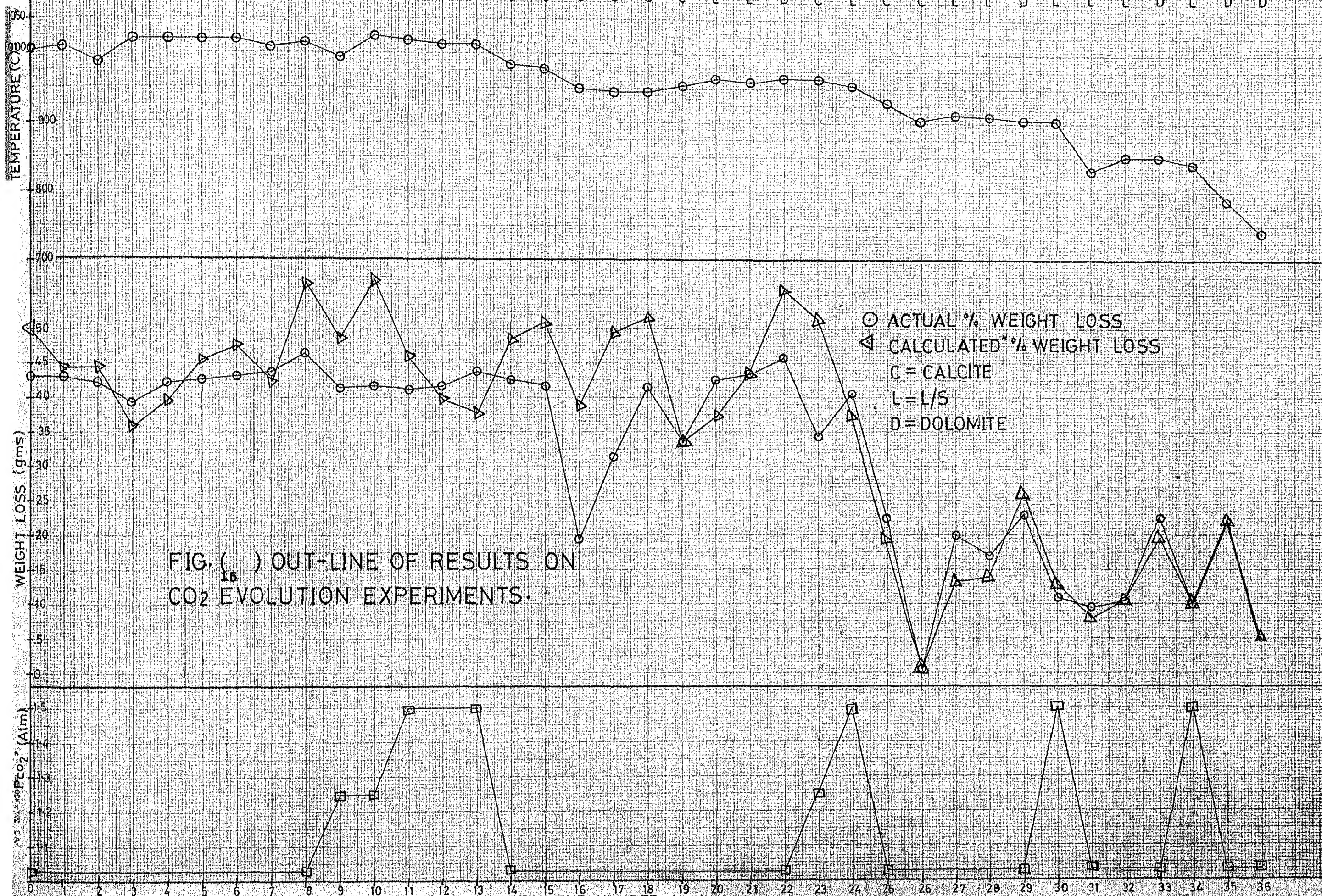
T A B L E IV-4

CORRECTED WEIGHT LOSS RESULTS ON CO_2 EVOLUTION EXPERIMENTS

Expt. No.	Weight loss at various time in gm					
	5 min	10min	15min	20min	25min	30min
CE0	0.23	4.52	8.00	10.15	11.65	12.65
CE1	1.69	5.25	7.93	10.07	11.41	12.41
CE2	3.51	7.66	9.07	10.54	11.48	...
CE3	4.55	7.72	9.06	9.87	10.41	10.57
CE4	3.39	7.21	8.66	10.33	11.08	11.40
CE5	3.15	8.05	10.68	11.48	11.64	...
CE6	6.29	9.78	11.79	12.06	...	...
CE7	6.36	11.45	13.59	14.13	...	...
CE8	8.38	12.24	13.31	13.42	...	...
CE9	.49	3.91	6.59	8.40	9.74	10.67
CE11	0.03	2.98	5.19	6.66	7.73	8.23
CE12	2.45	5.67	8.15	9.82	10.96	11.70
CE13	5.15	8.77	10.58	11.38	11.73	11.92
CE14	0.02	2.70	5.11	7.26	8.86	10.34
CE15	...	2.26	4.74	7.75	9.09	10.10
CE19	0.56	1.76	3.44	5.25	6.39	7.26
CE20	3.56	6.18	8.25	9.39	10.13	10.80
CE21	2.98	6.46	9.43	11.55	13.15	13.53
CE22	3.34	7.20	9.24	10.63	11.60	12.13
CE24	3.14	4.88	6.56	7.76	8.63	9.37
CE25	1.07	1.34	1.67	1.98	2.24	2.48
CE28	2.82	3.08	3.35	3.62	3.89	4.14
CE29	2.22	5.44	5.98	6.14	6.46	6.78
CE30	1.41	2.21	2.35	2.42	2.43	2.55
CE31	1.80	2.60	2.70	2.77	...	...
CE32	1.45	2.12	2.39	2.66	2.93	3.20
CE33	1.81	3.52	5.13	5.99	6.26	6.41
CE34	1.51	2.51	2.58	2.61	2.65	2.68
CE35	0.13	1.06	2.18	3.22	4.03	4.70
CE36	..	0.01	0.06	0.15	0.24	0.37
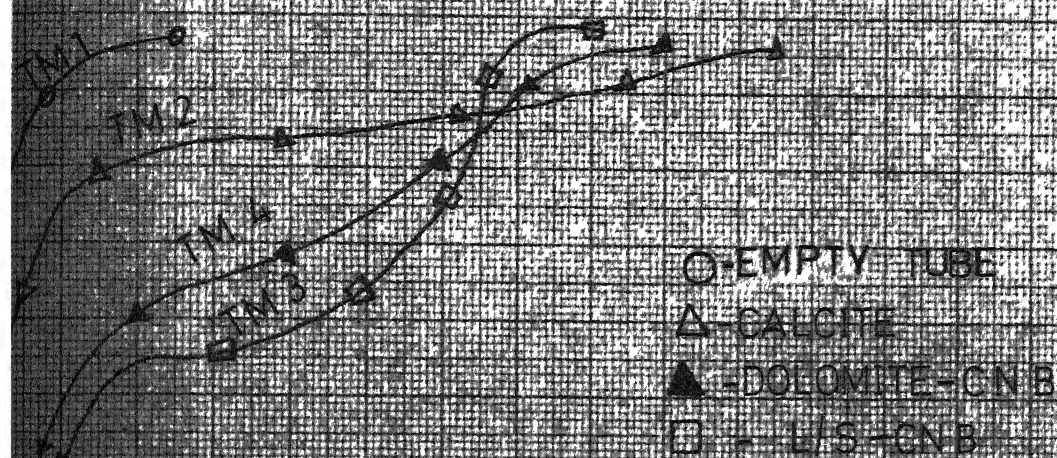
FIG.(16) TEMPERATURE MEASUREMENTS IN HEATING OF STATIC BEDS·
TOTAL(WEIGHT OF SAMPLE = 25 Gms)

O - EMPTY TUBE
△ - CALCITE
▲ - DOLOMITE - CN.B
□ - L/S - CN.B

Time (Minutes)

TM 20 & CE

TM 19 & CE

O - CALCITE
Δ - LIS CNB

TM 20 & CE

FIG.( ) MEASUREMENT OF
TEMPERATURE & CO₂ EVOLUTION
SIMULTANEOUSLY.

TM 19 & CE

CC/Sec

TIME (Minutes)
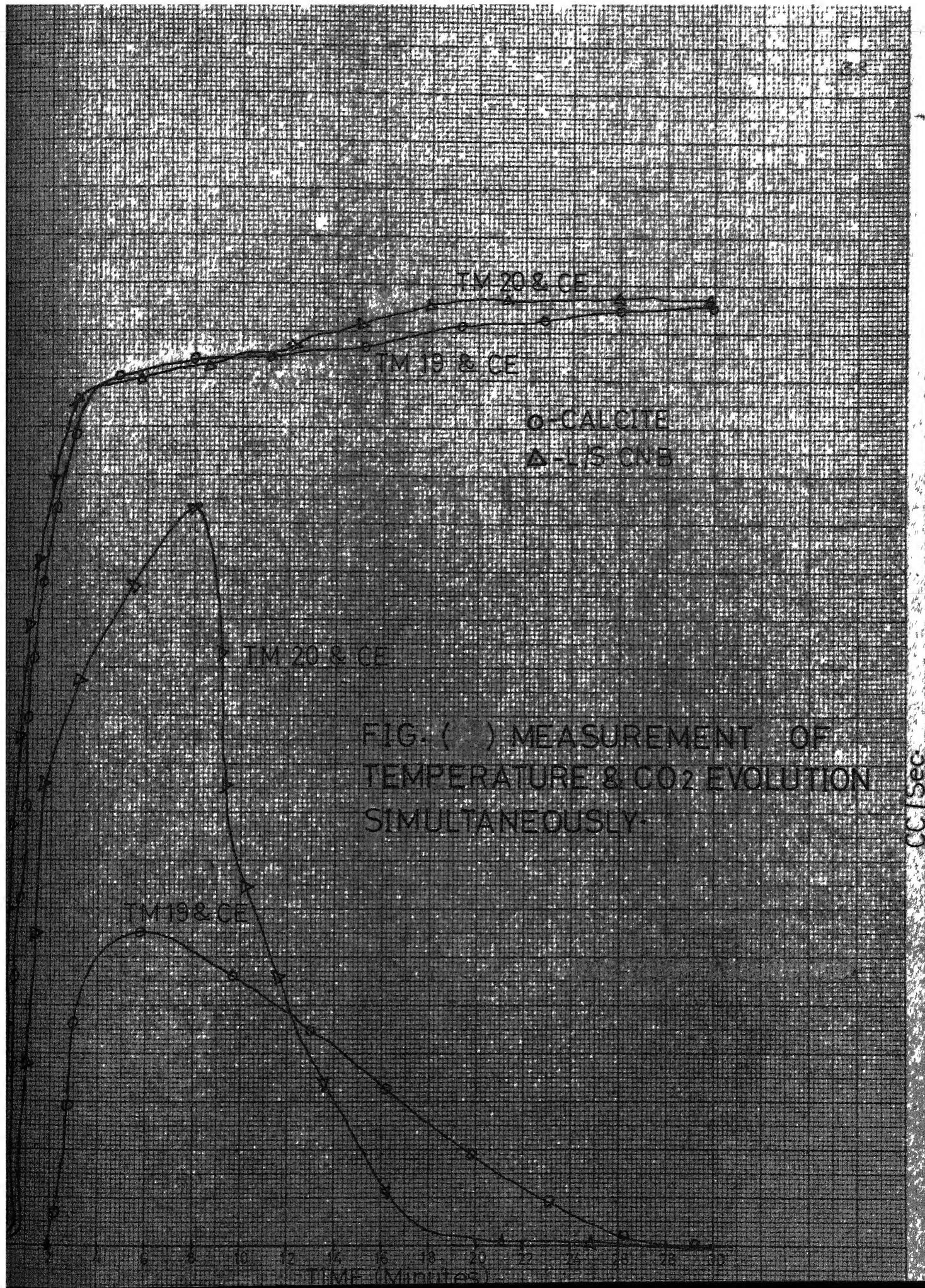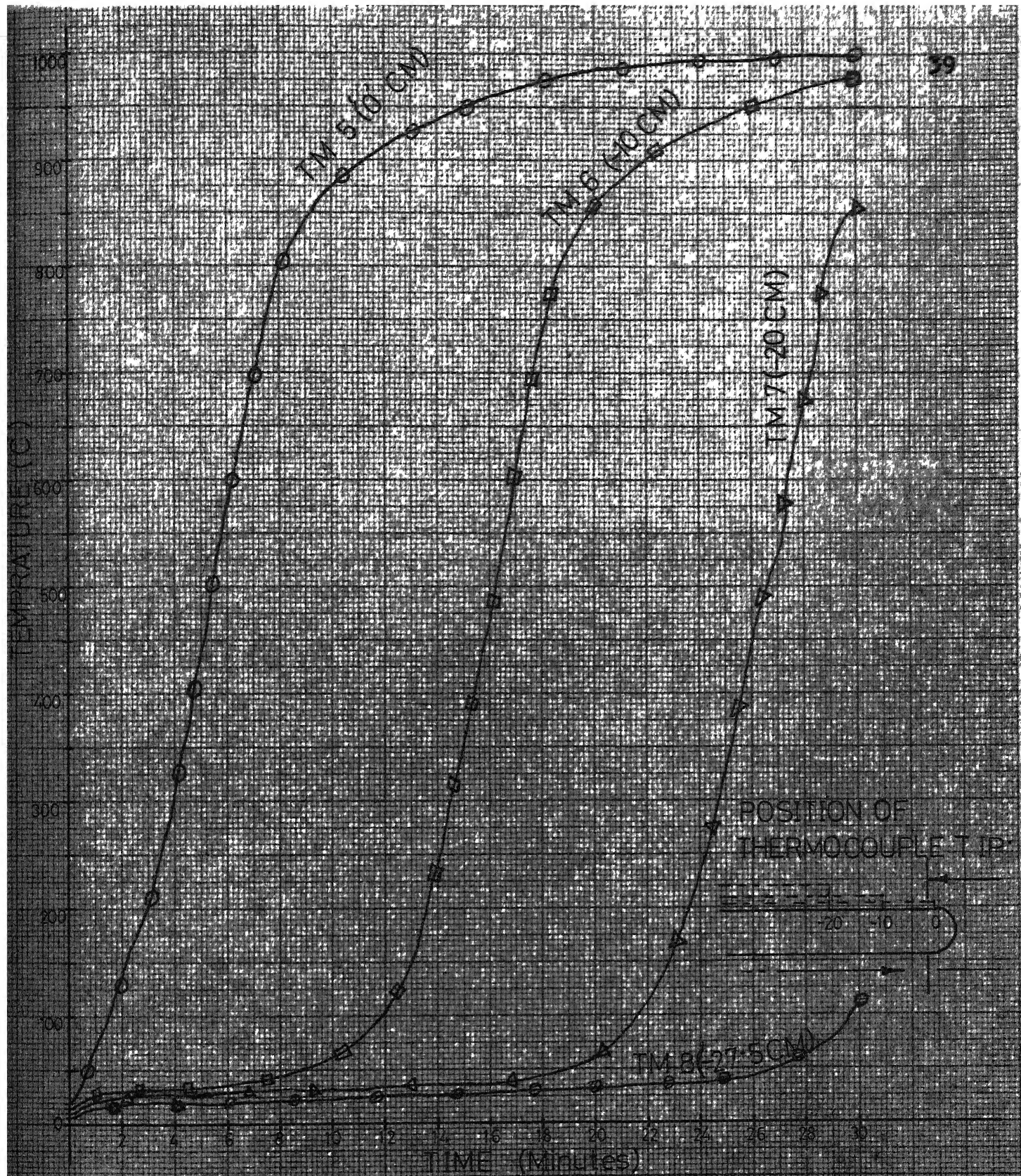
FIG. (   ) TEMPERATURE MEASUREMENTS IN A MOVING EMPTY TUBE.

BED SPEED = 1CM/MIN.
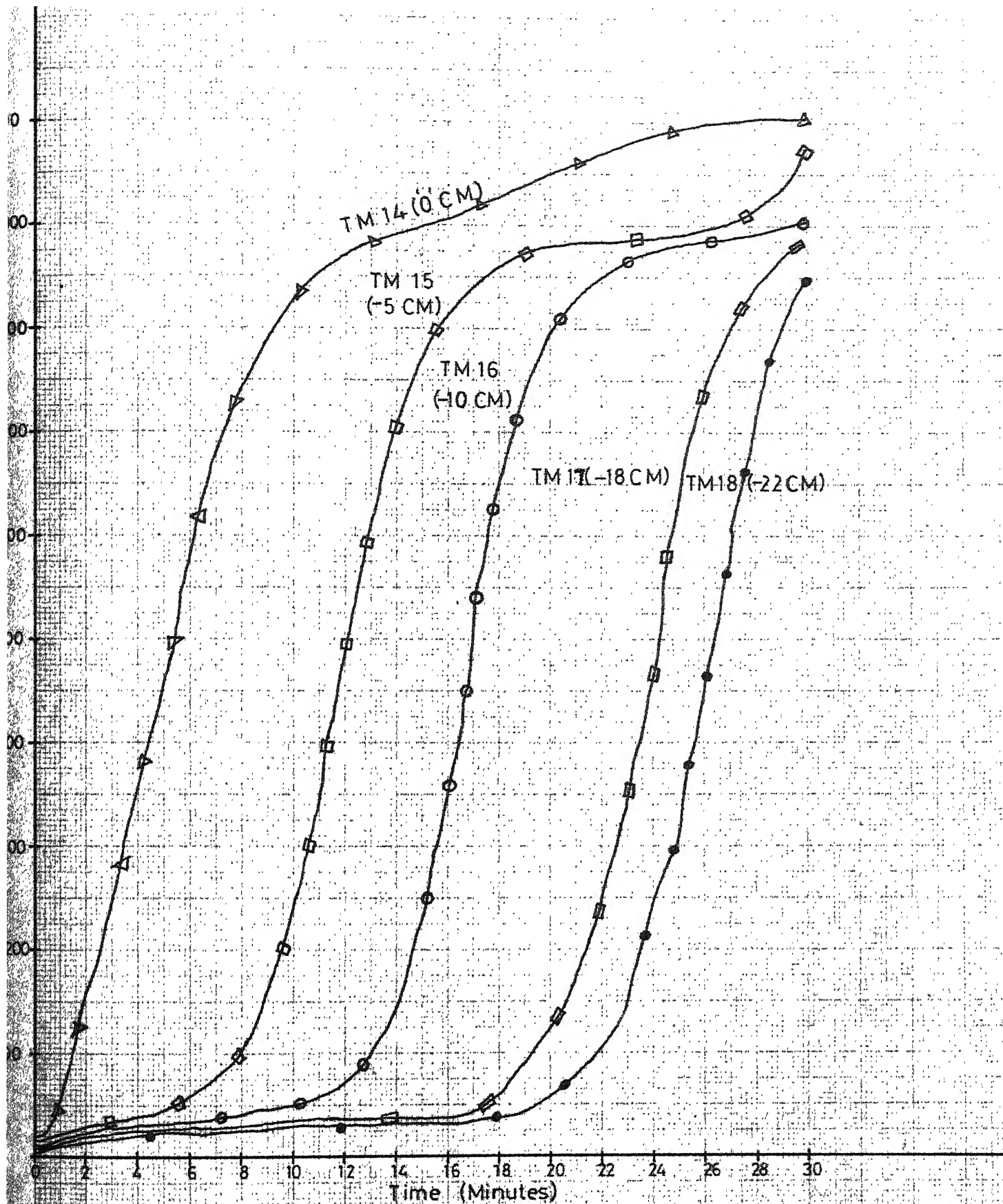
FIG.(20)TIME TEMPERATUR PLOTS
FOR L/S IN MOVING BED·
BED SPEED=1CM/Min)

C H A P T E R   V

D I S C U S S I O N

5.1 DTA Experiments :-

5.1.1 Standardization of experimental conditions for Thermal Analysis :

It is well known that thermo-analytical data are generally dependent on experimental conditions. These conditions include amount of sample weight, particle size, rate of heating, flow rate of gas, nature of packing etc. In the present work, the following standard conditions were maintained unless otherwise mentioned,

Weight of sample	=	400 mg
Particle size range	=	-90μ to $+63\mu$ (75u)
Heating rate	=	$25^{\circ}C/min$
Inert gas flow rate	=	1 cc/min
Nature of packing	=	5 taps on the crucible as standardized by the operator.

In many runs, particularly with calcite, calcination was not complete fig.(13) even when the maximum temperature of $1000^{\circ}C$ was reached. Some further calcination occurred during cooling of the furnace and it stopped when temperature fell below the decomposition temperature of $CaCO_3$. In such cases, the maximum loss in weight of the sample is found to be less than the theoritical value of 44 pct. for pure $CaCO_3$ decomposition. In other samples from mires presence of impurities such as SiO_2, Al_2O_3 and Fe_2O_3 in the sample may lead to lower values of percentage loss in weight than the theoritical values.

5.1.2 Dissociation of Carbonate mixtures:

When two carbonates are present together decomposition reactions *may or may not overlap. The exact decomposition behaviour will depend strongly on the nature of association of the carbonates. For example if the two carbonates are in the form of a mechanical mixture then each decomposition reaction represents decomposition of a pure substance. If however, these carbonates exist in the nature of a compound then the dissociation behaviour is more complex.

For example data in figures (11) and (12) for pure $MgCO_3$ and for pure $CaCO_3$ show that decomposition of $MgCO_3$ occurs at temperature about $500^{\circ}C$, that of $CaCO_3$ occurs at $900^{\circ}C$. A mechanical mixture of $MgCO_3$ and $CaCO_3$ for which data is given in fig.(8) shows two separate DTA peaks and TG plots as expected one corresponding to $MgCO_3$ at $600^{\circ}C$ and another corresponding to $CaCO_3$ at about $900^{\circ}C$. On the other hand dolomite is a compound of $MgCO_3$ and $CaCO_3$ and its decomposition is delayed due to its decreased activity in the compound DTA data in fig.(6) show that decomposition starts at temperature of $800^{\circ}C$ which is much above the decomposition temperature of $MgCO_3$. However once $MgCO_3$ has dissociated the $CaCO_3$ is no longer locked up in dolomite. Therefore the dissociation behaviour of $CaCO_3$ in dolomite will be same as in pure limestone.

Figures (9) and (10) show experimental data in another interesting system i.e. $Na_2CO_3.CaCO_3$. If a mechanical mixture *must occur in sequence. These sequential reactions

of sodium carbonate (Na_2CO_3) and $CaCO_3$ is heated there is no weight loss due to decomposition of Na_2CO_3 because it is thermo-dynamically stable upto $1200^{o}C$ even after melting at temperature of $850^{o}C$. The thermal analysis data shows an endothermic peak occur around $870^{o}C$ without any significant loss in weight. This peak therefore must ascribed to melting of Na_2CO_3. Decomposition of $CaCO_3$ in the mixture is delayed as it might have reacted with molten Na_2CO_3 to form a double compound $Na_2CO_3 \cdot CaCO_3$. Thermal analysis data for mechanical mixture of Na_2CO_3 and $CaCO_3$ and the compound $Na_2CO_3 \cdot CaCO_3$ are therefore comparable.

5.1.3 Dissociation behaviour of samples from Mines :-

In samples of limestone and dolomite collected from the various mines, some decomposition occurred at temperatures lower than $900^{o}C$, which can be due to presence of $MgCO_3$. This is clear from DTA and TG plots in figures (4) and (5), of runs DT1 to DT7 where results are summarized in Table IV-1. Results of DT5'A' and DT6'A' in Table IV-1 corresponds to decomposition of $MgCO_3$ in dolomite while DT5'B' and DT6'B' correspond to decomposition of $CaCO_3$ in the dolomite.

Dolomite sample from Chopan does not show any decomposition at temperature less than $900^{o}C$, as there is no corresponding peak for $MgCO_3$ in fig.(7). It is thus basically limestone. This demonstrates the utility of thermal analysis in identifying mineral constituents of ore sample.

5.2 Determination of Activation Energy from TG data :-

5.2.1 α - T plots :

Some of the TG data(weight loss) shown in Table IV-1 have been used to obtain α-T plots for dissociation of various samples. Here 'α' denots the fraction decomposed at any tempe-rature $T^{\circ}K$ and is otained as follows,

$$\alpha = \frac{\text{Actual weight loss}}{\text{Maxm. wt. loss corresponding to complete decomposition}} \quad --(4)$$

The value of α for these runs (DT1 to DT4 and DT12 to DT15) are summarized in Table V-1.

5.2.2 Analysis of non-isothermal data:

The basic equation of non-isothermal kinetic is obtained by combining three equations:

1. Kinetic law, $\dfrac{d\alpha}{dt} = kf(\alpha)$ ----------(5)

2. Arrhenius type equation,

     $k = A\exp(-E/RT)$ ------(6)

3. Temperature-Time equation,

     $T = f(t)$ -----(7)

For constant heating rate $\dfrac{dT}{dt} = B$ ----(8)

$$\frac{d\alpha}{f(\alpha)} = \frac{A\exp(-E/RT)dT}{B} \quad --(9)$$

Integrating, $\displaystyle\int_{0}^{\alpha}\frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_{0}^{T}\frac{A}{B}\exp(-E/RT)dT$ --(10)

Here 'α' denotes the degree of reaction (fraction decomposed) at time 't', 'A' and 'E' are kinetic parameters which satisfy an Arrhenius type equation. 'R' is the gas constant and 'B' is the heating rate(constant), g(α) and f(α) are function whose form is determined by the reaction mechanism. There are many

T A B L E V-1

CALCULATIONS OF FRACTION DECOMPOSED(α) VERSUS
TEMPERATURE FROM TG PLOTS OF DT EXPERIMENTS

Run No.	α at various Temperatures $^{\circ}K$					
	1073	1113	1173	1213	1253	1273
DT1	0.03	0.08	0.18	0.32	0.65	0.81
DT2	0.03	0.05	0.19	0.37	0.68	0.97
DT3	0.09	0.14	0.31	0.61	0.83	0.97
DT4	0.01	0.14	0.18	0.38	0.71	0.91
DT12	0.01	0.02	0.07	0.19	0.39	0.59
DT13	0.02	0.06	0.17	0.28	0.63	0.77
DT14	0.02	0.06	0.14	0.20	0.43	0.65
DT15	0.02	0.03	0.11	0.15	0.39	0.55

methods of solving this aquation all of which are approximate in nature. The most popular solution used frequently in the literature has been given by Coats and Redfern [11]. According to them if,

$$g(\alpha) = 1-(1-\alpha)^{1/3} = kt \quad ..(11)$$

and

$$f(\alpha) = 3(1-\alpha)^{2/3} \quad ....(12)$$

then,

$$\frac{1-(1-\alpha)^{1/3}}{T^2} = \frac{AR}{3BE}[1-2RT/E]exp[-E/RT] \quad \iota(13)$$

The value of activation energy is obtained by plotting $\ln[1-(1-\alpha)^{1/3}]/T^2$ versus $1/T$ for the case of $2RT/E \ll 1$.

Another method of calculating 'E' from non-isothermal kinetic data has been given by Ingraham [12] according to whom,

$$\ln[B\alpha/T^3] = E/RT \quad .. ..(14)$$

Activation energy 'E' in this case can be obtained by plotting $\ln[B\alpha/T^3]$ versus $1/T$. The calculated 'E' values using method of least squares for the above mentioned equations are summarized in Table V-2. Actual plots for the two equations for typical limestone and calcite materials are shown in fig. (28). Activation energy values of around 39 Kcal/mole obtained in Table V-2 are comparable to the reported value of 40.5 Kcal/mole [13] for single crystal study of calcite in vacuum.

5.3 Temperature Measurement and α-t(time) plots obtained from Moving bed experiments:-

Fig.(21) shows the α-t plots for some moving bed experiments described earlier. α values were obtained from the analysis (pct. XOI) of volume elements of the bed as stated in Table IV-2 as following,

48

T A B L E V-2

CALCULATION OF ACTIVATION ENERGY FROM TG DATA IN
DT EXPERIMENTS

Run No.	Coats + Redfern		Ingraham	
	Slope	'E' in Kcal /mole	Slope	'E' in Kcal /mole
DT1	+18680	-37.36	-18958	-37.92
DT2	+18995	-37.99	-19074	-38.15
DT3	+19138	-38.28	-19137	-38.27
DT4	+19086	-38.17	-19220	-38.44
DT12	+19043	-38.09	-19354	-38.71
DT13	+18965	-37.93	-19424	-38.85
DT14	+18875	-37.75	-19507	-39.01
DT15	+18797	-37.59	-19595	-39.19

Y-axis: $\ln\left[1-(1-\alpha)^{1/3}/T^2\right]$ or $\ln\dfrac{B\alpha}{T^3}$

X-axis: $1/T \times 10^{-4}$

Y-axis values: -20, -19, -18, -17, -16, -15, -14

X-axis values: 7, 8, 9, 10

Legend:

Method
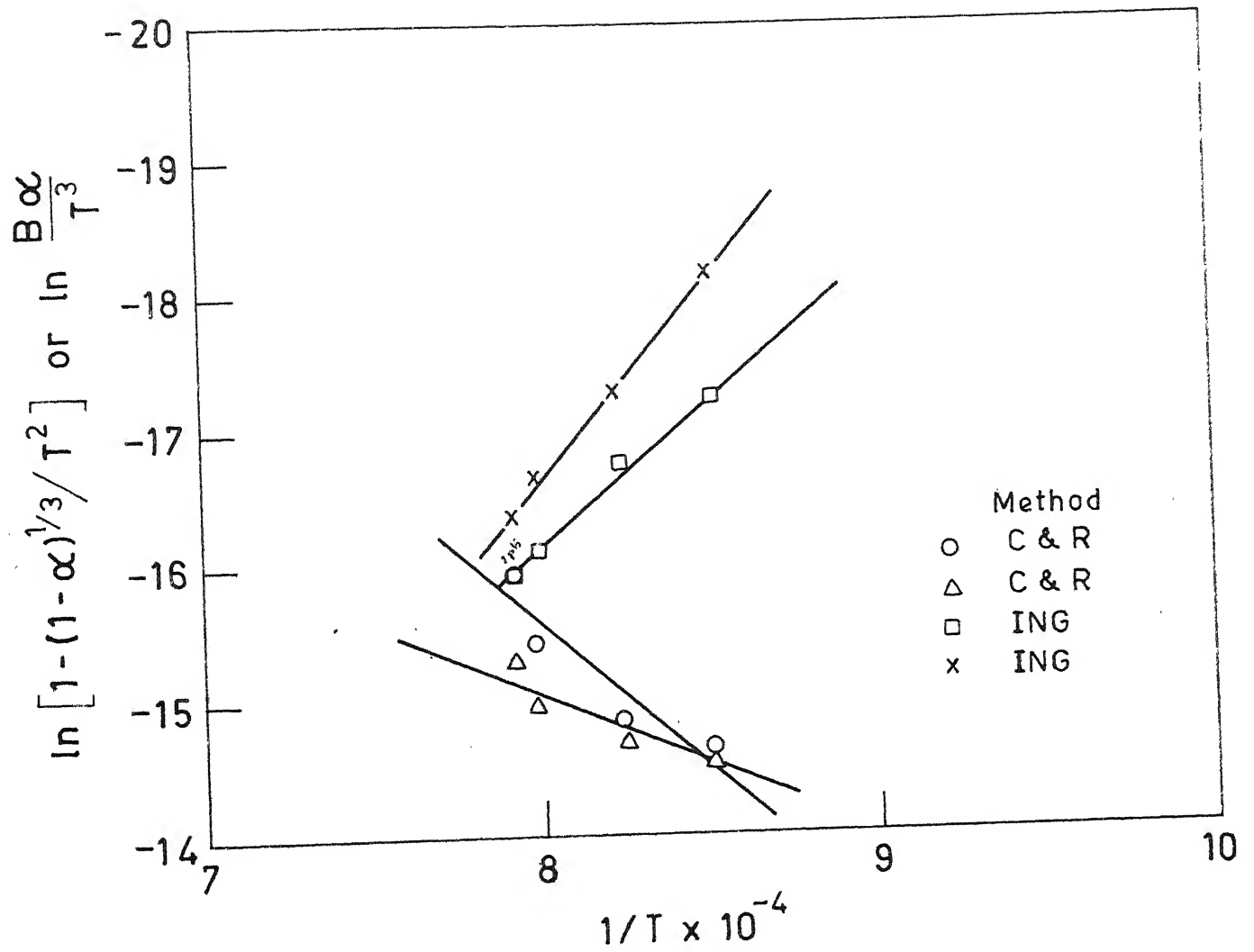- ◯ C & R
- △ C & R
- □ ING
- × ING

Fig. (28)   TYPICAL PLOTS FOR EQUATIONS OF COATS + REDFERN AND INGRAHAM FOR CALCULATION OF ACTIVATION ENERGY.
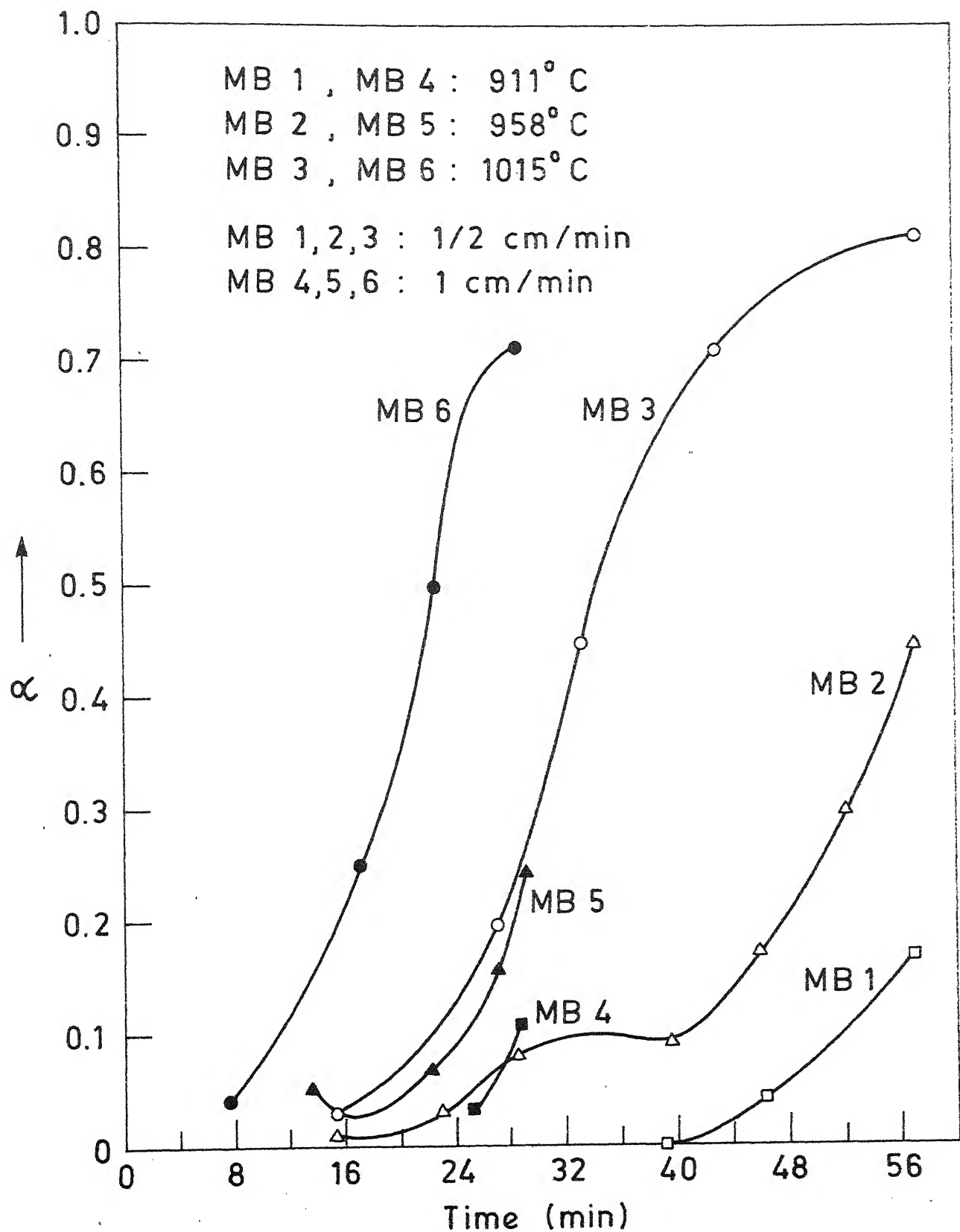
Fig. (21) α - TIME PLOTS FOR MOVING BED EXPE-
RIMENTS ON CALCITE.

$$\alpha \quad = \quad \frac{44 - \text{pct LOI}}{44} \quad \dots \quad (15)$$

At lower speed of bed, the materials will reach the high
temperature zone after a longer period and hence α-t plot will
shift to right as shown in fig. (21). As can be expected α-t
plots shift to left with increase in the furnace temperature.
These α-t plots may be further converted to α-T(temperature $^{\circ}K$)
plots for comparison with corresponding plots of DTA/TG experi-
ments in fig.(22).

Calcite samples in such experiments decompose to any appre-
ciable extent only near the entering end of the bed and the vol-
ume elements at some distances away practically remain undecom-
posed($\alpha < 10$ pct.). The length of the bed where appreciable amount
of decomposition occurs increses with increase in furnace tempe-
rature. In all these cases, complete decomposition of calcite
material did not occur even at the entering end. Degree of
decomposition decreased markedly with increasing distance from
the end. This phenomenon may be occurring due to following reasons.

1. Slow rate of calcite decomposition

2. Insufficient heating of bed length.

3. Retarding of decomposition by CO_2 evolved.

Experimental results on temperature measurements inside the bed
and CO_2 evolution measurements give more information on the
behaviour of calcite decomposition.

Fig.(23) and (24) described the variation of temperature
along the length of a moving bed at any time for limestone and

FIG·(22) COMPARISON OF ∠-T PLOTS OBTAINED FROM TG AND MOVING BED EXPERIMENTS FOR CALCITE MATERIAL·

FIG.( ) VARIATION OF TEMPERATURE OF THE BED WITH TIME FOR L/S·
(BED SPEED = 1 C·M/MINUTE)

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FIG( ) VARIATION OF TEMPERATURE OF BED WITH TIME FOR CALCITE BED SPEED = 1 CM/MINUTE.
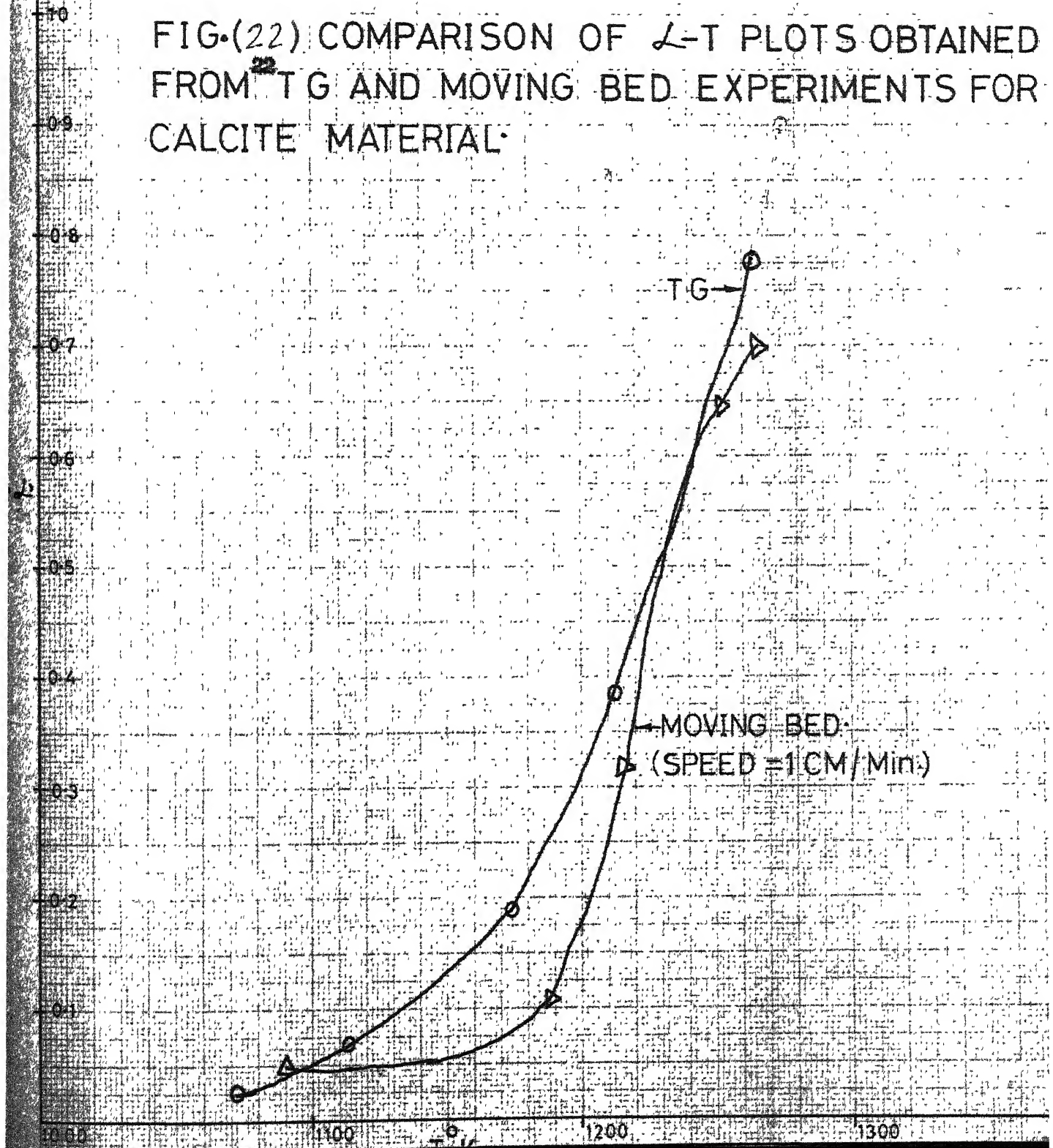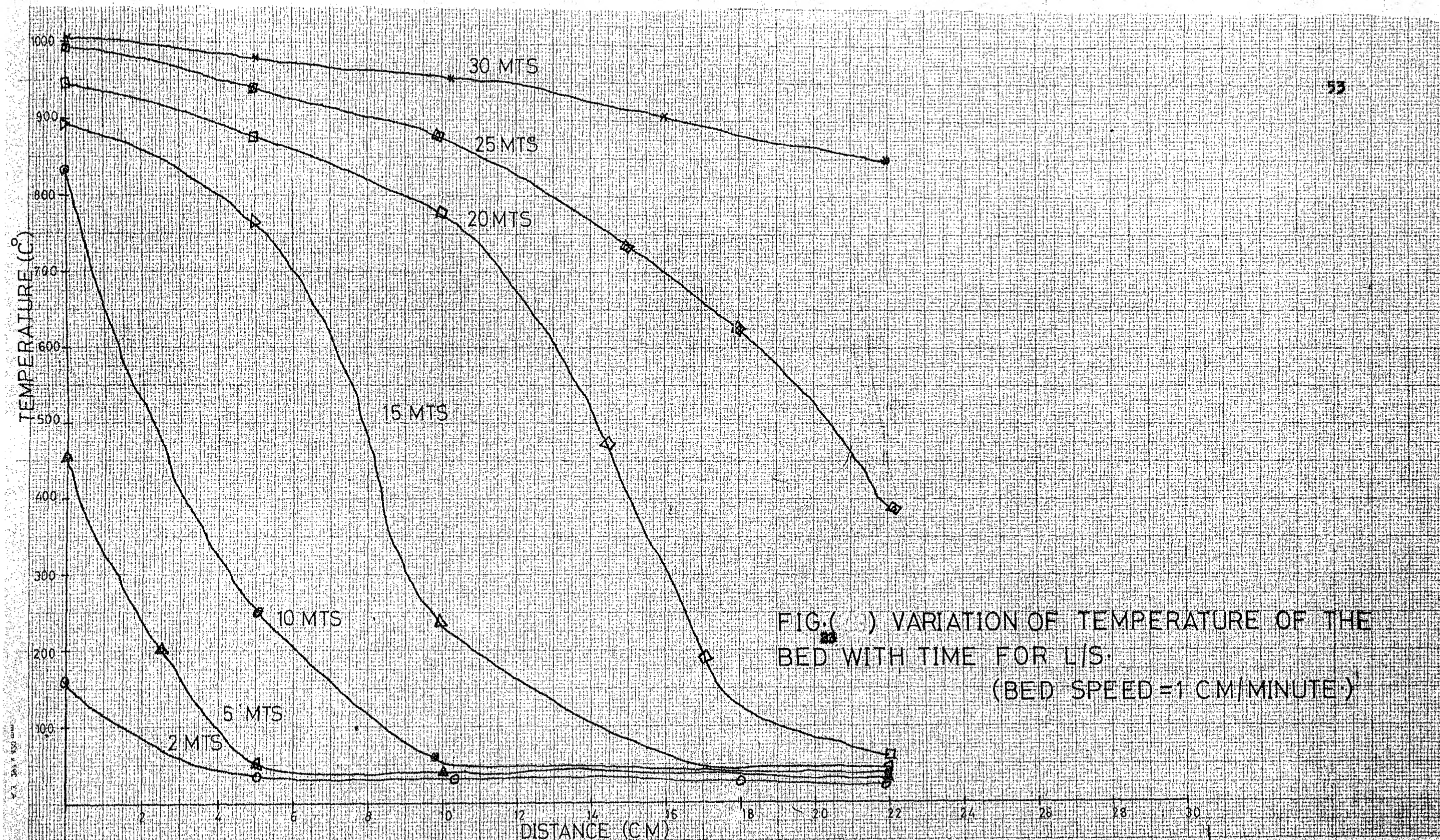
calcite. If is found that a steep temperature gradient prevails in the bed (moving at 1 cm/min) during the first twenty minutes of the experiment.

Since the decomposition temperature of calcite exceeds $900^{\circ}C$, only a small fraction in the bed will be decomposed within the duration of experiment. Actual rate of decomposition at any temperature will be further affected by variables such as nature of material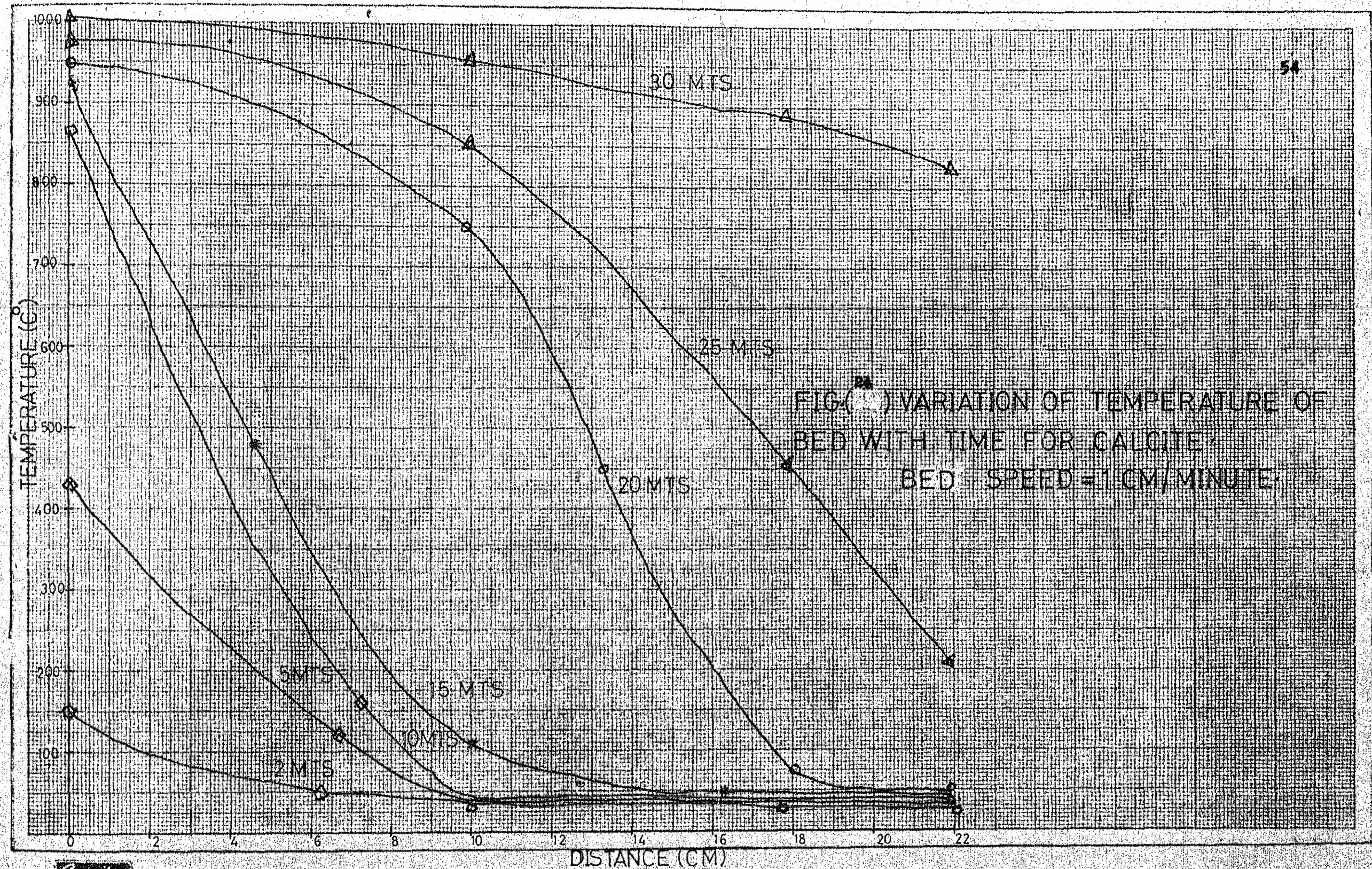, particle size, partial pressure of CO_2 etc. These factors have been separately studied on CO_2 evolution experiments described in Table III-3. Fig.(25) shows the effect of particle size for calcite and fig.(26) shows the effect of temperature for limestone and dolomite materials on rate of decomposition.

Experimental results on CO_2 evolution show the rate of decomposition is not markedly affected by partial pressure of CO_2 or particle size in the range studied in the present investigation. Retardation by CO_2 cannot account for steep $\alpha-t$ plots on moving bed experiment. It can be attributed only due to slow picking of temperature by the bed and slow rate of calcite decomposition. Similar experiments with commercial limestone and dolomite sample show marked increase in the rate of decomposition [fig.(27)] and they should result in greater degree of dissociation in the moving bed. It may also be noted that actual temperature of calcite, limestone or dolomite sample in the bed is much less than the furnace temperature, even when the whole mass is kept in the high temperature zone as shown by temperature measurements in static

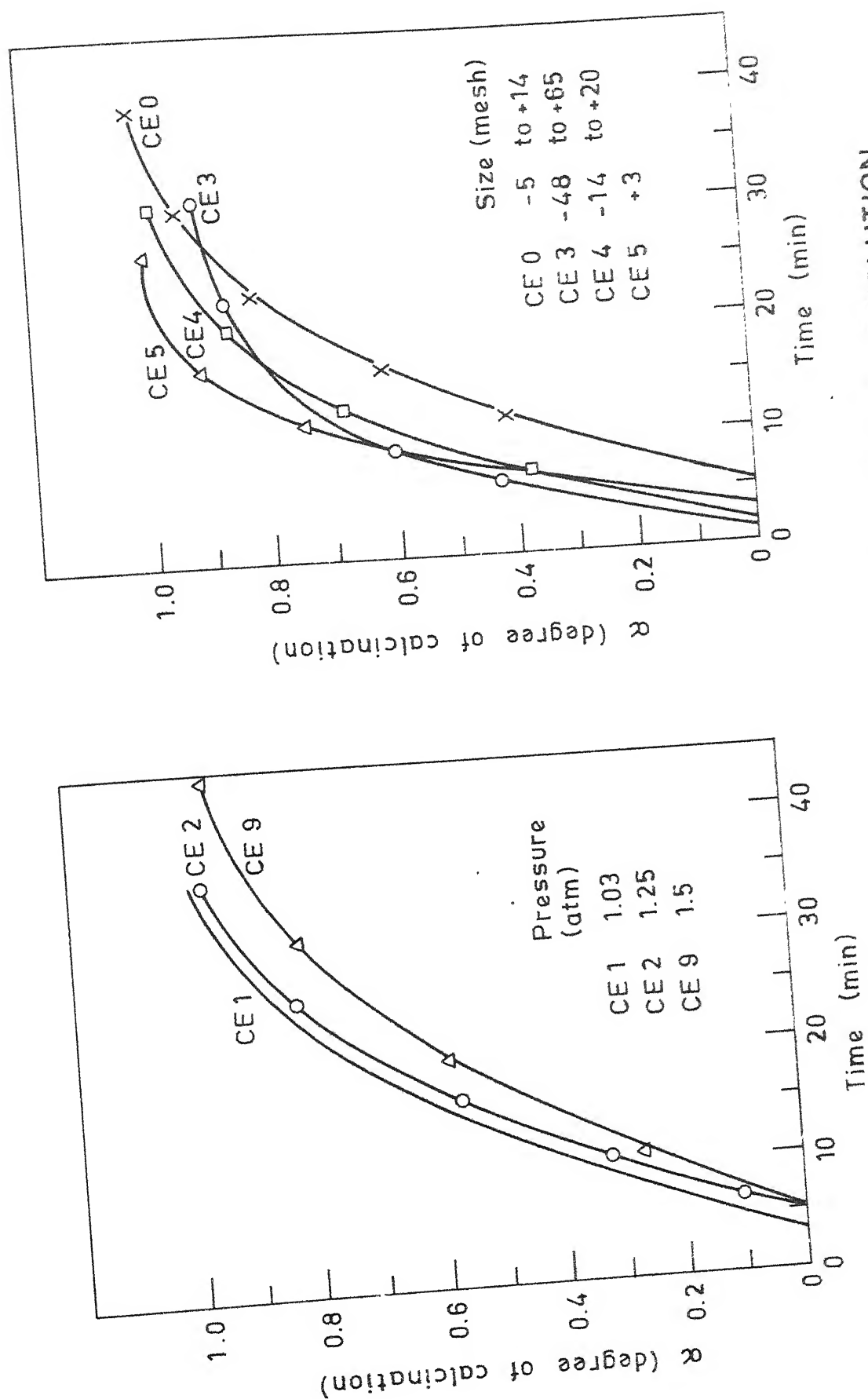Fig. (25) α - TIME PLOTS FOR CALCITE IN CO₂ EVOLUTION EXPERIMENTS.
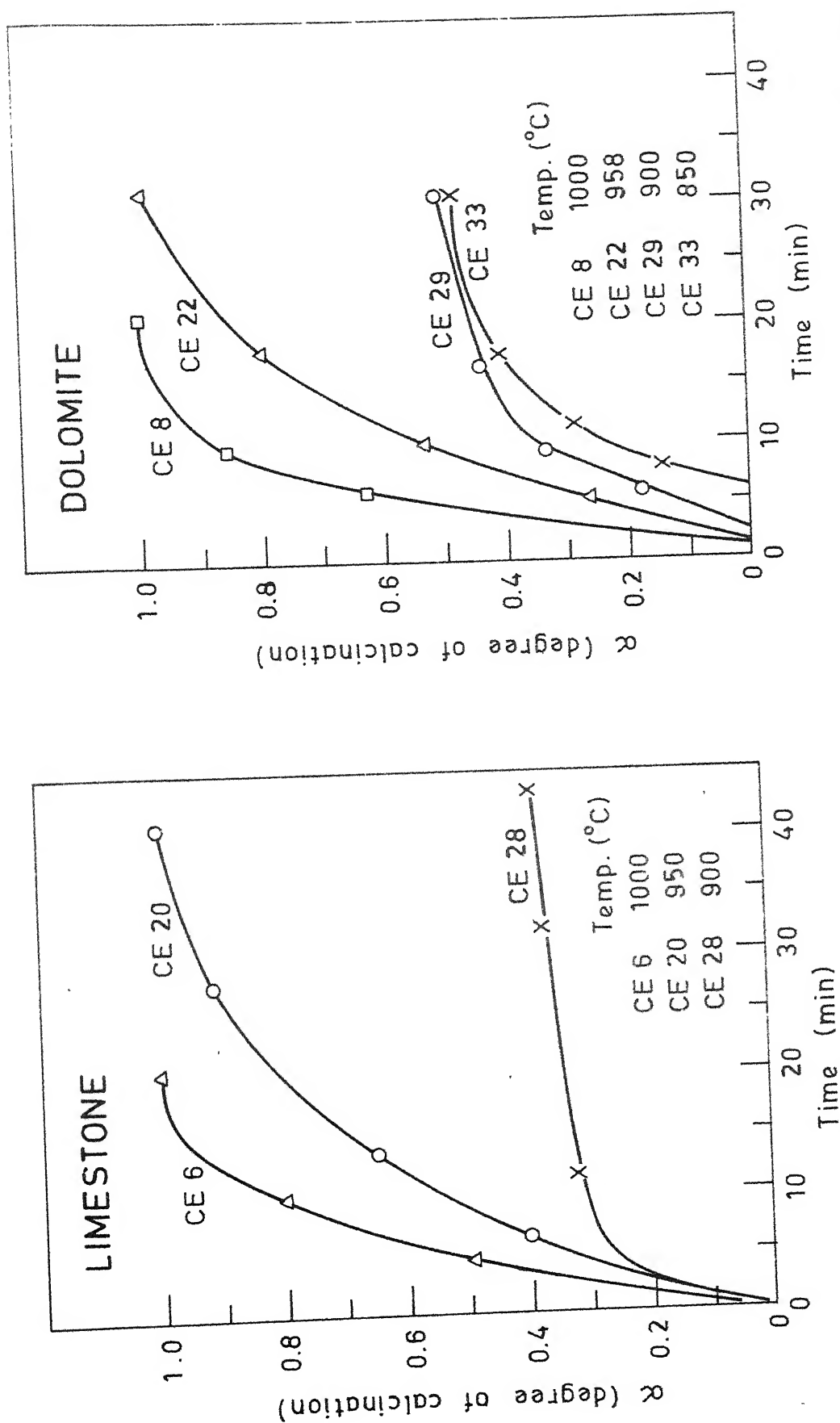
Fig. (26)   EFFECT OF FURNACE TEMPERATURE ON α-TIME PLOTS FOR
LIMESTONE AND DOLOMITE IN CO₂ EVOLUTION EXPERIMENTS.
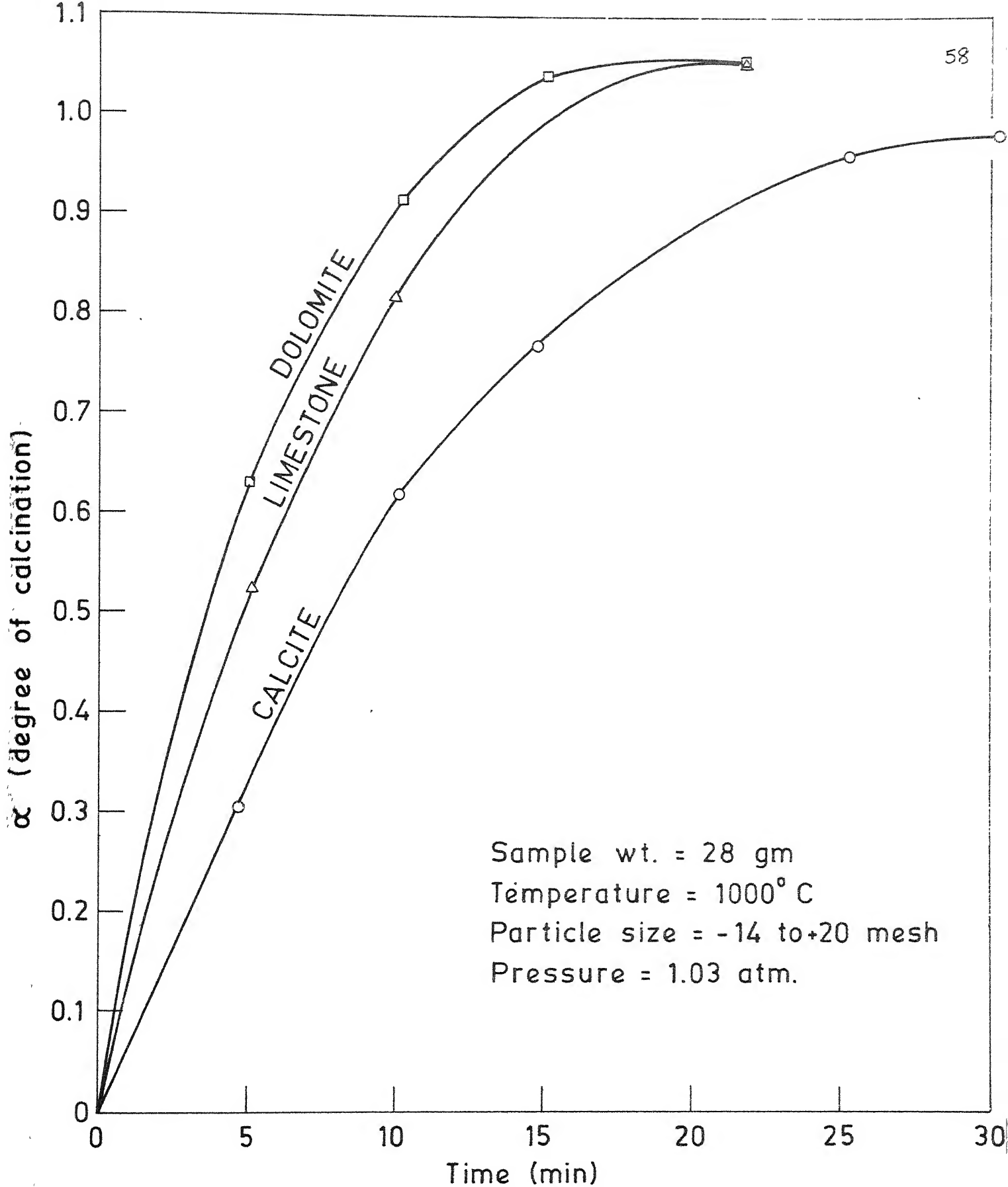
Sample wt. = 28 gm
Temperature = 1000° C
Particle size = -14 to+20 mesh
Pressure = 1.03 atm.

Fig. (27) α - TIME PLOTS FOR CALCITE, LIMESTONE AND DOLOMITE UNDER IDENTICAL CONDITIONS IN CO_2 EVOLUTION EXPERIMENTS.

bed experiments (TM1 to TM4). It will not be thus correct to calculate activation energy from α-t plots at different furnace temperatures. A simple heat balance model which predicts the temperature of the bed during its dissociation at any furnace temperature is described below.

5.4 Mathematical model for heating of carbonate materials in the Static bed :-

Let 'm' be the mass of the carbonate material and dm/dt is the rate of change of mass due to decomposition reaction, then from heat balance one can write,

$$\frac{d}{dt}\int_{298}^{T+273}(m,Cp_s)dT = hA(T_f-T) - \Delta H_R(-dm/dt) - \int_{298}^{T+273}Cp(\frac{dm}{dt})dT \quad .(16)$$

where Cp_s is specific heat of solid and Cp is specific heat of CO_2 evolved, T is temperature in ^oC, h is heat transfer coefficient in Cal/cm^2 ^oC min, ΔH_R is heat of decomposition reaction in (960 Cal/gm of CO_2 produced for $CaCO_3$ decomposition) T_f is furnace temperature in ^oC, 'A' is surface area of solid material in the tube. In deriving equation(16), the sample is assumed to be uniform temperature throughout and it is kept in the constant temperature zone of the furnace.

Consider the case where the material is not decomposing

Case I :- $T < T_{reaction}$ and $dm/dt = 0$, and taking specific heat to be constant for samples,

$$mCpdT/dt = hA(T_f-T) \quad ......(17)$$

Rearranging and integrating the equation(17)

$$\int_{T_f-T}^{T} \frac{dT}{T_f-T} = \int_{c}^{t} hA/mCp.dt \qquad \ldots\ldots\ldots(18)$$

$$\ln \frac{T_f-T_A}{T_f-T} = hA/mCp.t \qquad \ldots\ldots\ldots(19)$$

$T_{reaction}$ is $900^{\circ}C$ for calcite material. $T_{reaction}$ will be lower for material like limestone and dolomite which contain $MgCO_3$. Value of 'h' for heating of material in a furnace has been reported to be* 0.16 $Cal/cm^2.{}^{\circ}C.min$ (AppA). Values of m, A, Cp, T_f and T_A are known from experimental conditions.

Results of calculation show that 25 gm of calcite material in the tube will get heated to decomposition temperature of $900^{\circ}C$ in $1\frac{1}{2}$ minutes when kept inside the furnace at $1000^{\circ}C$. This agrees with the results of actual temperature measurement in the static bed in fig.(16).

Limestone and dolomite materials contain a fraction of $MgCO_3$ which decompose at temperature lower than $900^{\circ}C$. The rate of heating will be less due to endothermic decomposition of $MgCO_3$ in such cases as dm/dt cannot be neglected any more in equation(17). Value of dm/dt depends upon the amount of undecomposed material left in the tube as well as on temperature of material. Since temperature changes with time, this is essentially a case of non-isothermal decomposition which is discussed below.

Case II : $T > T_{reaction}$,   dm/dt $= f(T,$ carbonate mass left)
Assuming specific heats of species to be constant at temperature, equation(16) can be rewritten as,

$$mCp_s\frac{dT}{dt} + Cp_s T\frac{dm}{dt} = hA(T_f-T) - \Delta H_R(-\frac{dm}{dt}) + Cp_{CO_2}(\frac{dm}{dt})T\ldots\ldots(20)$$

* (see Appendix A)

T A B L E V-3

CALCULATIONS OF CONSTANT TEMPERATURE IN STATIC BED FOR DIFFERENT RATE OF CARBONATE DECOMPOSITION

$$T_f = 1000^\circ C$$

dm/dt gm/min	Theoritical flow rate(cc/sec)	Calculations for $CaCO_3$		Calculations for $MgCO_3$	
		T_f-T	$T(^\circ C)$	T_f-T	$T(^\circ C)$
0.05	0.5	8	992	5	995
0.10	1.0	13	987	7	993
0.20	1.9	27	973	15	985
0.30	2.8	41	959	24	976
0.40	3.7	54	946	31	969
0.50	4.7	68	932	39	961
0.60	5.6	82	912	47	953
0.70	6.5	95	905	55	945
0.80	7.5	109	891	61	959
0.90	8.4	123	871	71	929
1.00	9.3	136	864	79	922

presence of $MgCO_3$ will also affect the heat balance calculations due to its lower value of heat of decomposition i.e. 24.25 Kcal/ mole compared to 42.5 Kcal/mole of $CaCO_3$ decomposition. At the same temperature of sample, higher rates of decomposition of $MgCO_3$ can be obtained than predicted for $CaCO_3$ as shown in Table V-3. Calculated temperature values compare well with the measured values.

When practically all carbonates have decomposed |dm/dt| will again be zero and equation(19) will described the further rise in temperature of the sample. Calculations show that the calcine limestone or dolomite sample will get heated from a temperature of 910°C to 990°C in 1 minute. Details are given in Table V-4. In actual practice it takes much larger time of 6 to 8 minutes because there will be a small fraction of carbo- nate material decomposing even at temperature higher than 910°C and it will consume heat in the process.

$$T \ A \ B \ L \ E \quad V-4$$

DETAILS OF CALCULATIONS FOR HEATING OF DECOMPOSED
SAMPLE IN THE FURNACE

Specific heat Cp_{CaO}	=	11.7 Cal/mole.^{o}C
	=	0.21 Cal/gm.^{o}C
Surface area(A) of the Sample	=	43.96 cm^2
Initial mass	=	25 gm
Decomposed mass(m)	=	15 gm
Heat transfer co-efft. h=		0.16 Cal/cm^2.^{o}C.min
Temperature of furnace T_f=		1000°C
Initial temp. of sample = T_A		910°C
Final temp. of sample T =		990°C

$$\ln[T_f-T_A/T_f-T] \quad = \quad hAt/mCp$$

$$\ln[1000-910/1000-990] \quad = \quad \frac{0.16 \times 43.96 \times t}{15 \times 0.21}$$

$$2.2t \quad = \quad 2.2$$

$$t \quad = \quad 1 \ min$$

5.5 Model for heating of carbonate materials in Moving bed :-

It is possible to set up a simple heat balance equation for volume elements of length Δl, in the moving bed also. For any volume element at time t for Case I of no decomposition,

$$\pi r^2 \Delta l.\rho CpdT/dt = 2\pi rh\Delta l(T_f - T) \quad \ldots\ldots(22)$$

Where r is the radius of tube, ρ is bulk density of the sample, T_f is the temperature of furnace corresponding to the volume element. Temperature is assumed to be constant across the cross section of tube and conduction terms in the axial direction are neglected.

Simplifying equation(22)
$$\frac{dT}{T_f - T} = \frac{2h}{r\rho Cp}dt \quad \ldots\ldots\ldots(23)$$
Therefore,
$$\int_{T_0}^{T} \frac{dT}{T_f - T} = \frac{2h}{r\rho Cp}\int_{0}^{t} dt$$
$$= 2ht/r\rho Cp \quad \ldots\ldots(24)$$

For stationery beds, the left hand integral could be easily evaluated because T_f was constant. For a *temperature T_f is not constant but varying according to the temperature profile of the furnace. The integral can be evaluated if the variation of T_f is precisely known. If the bed is moving at the uniform velocity v, then
$$v = x/t \quad \ldots\ldots(25)$$
where x is the distance covered in time t. The temperature profile of the furnace may be expressed in following form,

$$T_f = T_0 + (T_m - T_0)(1 - \exp{-jx}) \quad \ldots(26)$$

where T_0 is the temperature of the furnace mouth. T_m is maximum temperature of furnace and j is a constant. This shows that the evaluation of the left hand side integral in equation (24)
*volume element in a moving bed, the surrounding furnace)

would be somewhat complicated.

Calculations are further complicated in Case II where decomposition of limestone is also occuring, CO_2 gas so evolved passes through the rest of the bed and affects the overall heat balance in the volume element. The exact analysis for decomposition of carbonates in the moving bed are therefore not carried out in this thesis.

C H A P T E R   VI
C O N C L U S I O N

It is sh wn that thermal analysis(simultaneous measurement of DTA, TG and DTG) can be used for reliable characterization in terms of the minerological composition and impurity content of the carbonate samples. DTA of dolomite indicates two endothermic peak corresponding to sequential decomposition of $MgCO_3$ and $CaCO_3$. The $MgCO_3$ peak in dolomite however occurs at a temperature($800^\circ C$) higher than that associated with pure $MgCO_3$ ($550^\circ C$). The TG data for the non-isothermal decomposition of carbonate has been analyzed to obtain the kinetic parameters for the reaction mechanism. Calculated values of activation energy around 39 Kcal/mole are comparable with the reported value of 40.5 Kcal/mole in the literature.

2. In the moving bed experiments, calcite material decomposes to any appreciable extent only at the entry of the entry of the bed only and degree of dissociation decreases markedly with distance away from that end. This phenomenon is explained due to temperature variation in the bed.

3. A technique of measuring the flow of CO_2 gas evolved during decomposition reaction under controlled temperature and pressure has been developed in the present work. It has been shown that limestone and dolomite materials dissociate much faster than calcite material under identical conditions of temperature and pressure. CO_2 pressure in the range of 1 to 1.5atm.

and the particle size in the range from -3mesh to +65mesh donot seem to affect the rate of decomposition of calcite.

4. Actual measured temperature of calcite, limestone and dolomite samples in static bed experiments are always less than the furnace temperature. Heating of these materials in the furnace is characterized by an attainment of nearly constant temperature for some time. Constant temperature value for limestone and dolomite samples are much less than the temperature of the calcite samples. A heat balance model has been developed to corelate the temperature of the bed with the rate of decomposition of the carbonate material and the results have been confirmed by actual measurement of temperature in the static bed as well as in the moving bed.

R E F E R E N C E S

[1] - R.K. Verma, Optimum degree of Direct reduction and Gas
utilisation towards minimum coke rate in a B/F, M.Tech.
Thesis, IIT/Kanpur, 1980.

[2] - Harold E.McGanon(Editor), Making, Shaping and Treating of
Steel, U.S. Publication - 1971 edition.

[3] - Boyton Roberts, Chemistry and Technology of Lime and
Limestone, 1964.

[4] - H.K. Linzell etal, The loss in weight of limestind as a
function of time and temperature of burning, Proc. Am.
Inst. of Chem. Engg., 1926.

[5] - R. Hedin, Changes occuring in limestond during heating
before calcination, Sweden Concrete Research Inst. Billetin,
23, p34, 1954.

[6] - R.S. Fostel, Research Report to the National Lime Associa-
tion, M.I.T., 1964.

[7] - H.S. Ray, Kinetic studies under rising temperature condi-
tins using small and large samples, Dept. of Met. Engg.,
IIT/Kharagpur, Private communication.

[8] - Dr. G.L. Liptay(Editor), Atlas of Therm.-Analytical curves
(TG, DTG, DTA curves measured simultaneously), 1971.

[9] - F. Paulik, J. Paulik and L. Erdey, Derivatgraph, Operating
Instruction System, Manual, 1971.

[10] - H.S. Ray, Non-Isothermal kinetics theory and applications,
Met. Engg. Dept., IIt/Kharagpur, Private communication.

[11] - A.W. Coats and J.P. Redfern - Nature Vol. 201, p68, Jan. 1964.

[12] - T.R. Ingraham in H.G. McAdie, Ed. Proc., Second Toronto symposium on Thermal Analysis, Toronto section of Chemical Instt. of Canada, p29, Feb. 27, 1967.

[13] - Elizebath K. Powell and Alan W. Search, The Rate and Activation Enthalpy of Decomposition on $CaCO_3$, Met. Trans. Vol. II/B, Deptember, 1980.

[14] Reinhardt Schumann, Met. Engg. Principle Vol I, M.I.T., 1952.

[15] Harold E.McGanon(Editor), Making, Shaping and Treating of Steel, p292, U.S. Publication, 1971 edition,

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A P P E N D I X - A

CALCULATION OF HEAT TRANSFER COEFFICIENT FOR HEATING OF CARBONATE MATERIALS IN THE FURNACE

It is given in reference[14] that the value of heat transfer coefficient for heating of bricks in the furnace at $1000°F$ is 10 $Btu/hr.ft^2.°F$. This value includes the contribution due to convection as well as due to radiation. In the present work temperature of furnace is $1000°C$ or $1830°F$. Contribution due to radiation is going to be more and the value of 'h' will increase $h = h_c + h_r$

Taking h_c as 5 $Btu/hr.ft^2.°F$ and h_r as 5 $Btu/hr.ft^2.°F$ at $1100°F$, h_r value at $1830°F$ can be calculated as follows,

$$h_r(1830)/h_r(1100) \quad =[1830+460/1100+460]^3$$
$$= 3.0$$
$$h_r(1830) \quad = 3 \times 5 = 15 \ Btu/hr.ft^2.°F$$
$$h(1830) \quad = h_c + h_r$$
$$= 5 + 15 = 20 Btu/hr.ft^2.°F$$
$$= 0.16 \ Cal/cm^2.°C$$

This value is only approximate in nature and in actual practice it will vary with temperature of sample as well as with the presence of CO_2 in the tube.

A P P E N D I X - B

<u>DETAILS OF SPECIFIC HEATS OF SPECIES OF INTEREST
IN THE PRESENT WORK [15]</u>

Species	$Cp = a+bT-CT^2$ (cal/mole.$^\circ K$)			Cp in cal/gm.$^\circ C$				
	a	$b \times 10^3$	$C \times 10^5$	100°C	300°C	500°C	700°C	900°C
CO_2	10.57	2.10	2.06	0.22	0.25	0.27	0.28	0.29
CaO	11.67	1.08	1.56	0.20	0.21	0.22	0.23	0.23
$CaCO_3$	24.98	5.24	6.20	0.22	0.26	0.28	0.29	0.31
MgO	10.18	1.74	1.48	0.24	0.27	0.28	0.29	0.30
$MgCO_3$	18.62	13.80	4.16	0.25	0.30	0.34	0.38	0.41

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